ENGINEERING
LIBRARY

DEC 18 1946

RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XIX NUMBER 4

October, 1946

Published Quarterly under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY
at Prince and Lemon Sts., Lancaster, Pa.

The furnace-process reinforcing carbon black (HMF type) for synthetic and natural rubber. Easy processing; smooth and rapid extrusion; full reinforcement; low heat build-up; high resiliency; high resistance to cut growth, flex cracking and abrasion. Excellent for blending with channel black in GR-S tread stock to secure better plasticity.

UNITED CARBON COMPANY, INC.

CHARLESTON, WEST VIRGINIA

New York – Akron – Chicago

RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XIX NUMBER 4

October, 1946

Published under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY

B B B B B B B B B B B B B B B B

B

IS FOR:

Better mixing
Better curing
Better aging
Better detrition
Better tire life

STATEX-B

for Better compounding

MICRONEX
For 30 years—The Standard Reinforcing Carbon

FURNEX
The High Resilience Carbon

STATEX-93
The Carbon for Heavy-duty Reinforcement

• COLUMBIAN COLLOIDS •

COLUMBIAN CARBON CO. • BINNEY & SMITH CO.
MANUFACTURER DISTRIBUTOR

400 TONS OF SMOKE A DAY

RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Division of Rubber Chemistry of the American Chemical Society,
Prince and Lemon Streets,
Lancaster, Pa.

Editor ..... C. C. DAVIS
Advertising Manager ..... S. G. BYAM
Secretary ..... C. R. HAYNES
Treasurer ..... C. W. CHRISTENSEN

Vol. XIX October, 1946 No. 4

CONTENTS

General Section PAGE

Officers iii
Spring Meeting of the Division of Rubber Chemistry of the American Chemical Society vi
New Books and Other Publications xi

Reprinted Papers

Report of Conference on Postwar Preparation and Packing of Rubber 865
Influence of Vulcanization on the Oxidability of Rubber. II. Vulcanizing Agents other than Sulfur. JEAN LE BRAS 876
Vulcanization Reactions in Butyl Rubber. Action of Dinitroso, Dioxime, and Related Compounds. JOHN REHNER, JR., AND PAUL J. FLORY 900
Evaluation of the Physical Properties of Rubber Vulcanizates at Low Temperatures. L. MULLINS 915
Hardness Tests at Low Temperatures. PAUL LAINÉ AND ANDRÉ ROUX 933
The Influence of Milling on the Plasticization of Rubber. ADRIEN HAEHL AND JEAN LE BRAS 938
The Accelerated Vulcanization of Ebonite. B. L. DAVIES 948
A Study of the Rubber-Metal Bond. S. BUCHAN 956
Chemical Nature of the Rubber-to-Brass Bond. S. BUCHAN 968
The Mobility of Foreign Molecules Dissolved in Rubber. JEAN HAEGEL 987
The Statistical Length of Long-Chain Molecules. L. R. G. TRELOAR 1002
The Elasticity of a Network of Long-Chain Molecules. III. L. R. G. TRELOAR 1009
The Course of Autoöxidation Reactions in Polyisoprenes and Allied Compounds. XI. Double-Bond Movement During the Autoöxidation of a Monoölefin. E. HAROLD FARMER AND DONALD A. SUTTON 1022
Preparation and Properties of Rubberlike High Polymers. I. Polymerization of Dienes and Vinyl Compounds in Bulk. C. KONINGSBERGER AND G. SALOMON 1029
Elastic Deformation and Molecular Weight in Polyisobutylene. JOHN REHNER, JR. 1047
Applications of Ultraviolet Spectrography. A Study of Some Accelerators. CHARLES DUFRAISSE AND JEAN HOUPILLART 1051
Applications of Ultraviolet Spectrography. A Study of the Transformations Which Tetramethylthiuram Disulfide Undergoes During the Vulcanization Process. ANDRÉ JARRIJON 1061

Spectrophotometric Determination of the Styrene Content of Butadiene-Styrene Copolymers. E. J. MEEHAN 1077
The Hertzian Spectrum of Rubber and Its Micellar Constitution. PIERRE GIRARD AND PAUL ABADIE 1085
An X-Ray Study of Some Synthetic Elastomers. Polychloroprenes. HENRI FOURNIER AND JEAN JACQUES TRILLAT 1088
The Structure of Some Synthetic Elastomers. Ethylene Polysulfide. JEAN JACQUES TRILLAT AND ROBERT TERTIAN 1090
The Terminology of Intrinsic Viscosity and Related Functions. L. H. CRAGG 1092
The Theory of Permanent Set at Elevated Temperatures in Natural and Synthetic Rubber Vulcanizates. R. D. ANDREWS AND A. V. TOBOLSKY 1099
Applications of Infrared Methods in the Structural Examination of Synthetic Rubber. J. F. FIELD, D. E. WOODFORD, AND S. D. GEHMAN 1113
The Proportion of Crystalline and Amorphous Components in Stretched Vulcanized Rubber. A. J. WILDSCHUT 1124
Significance of the Equation of State for Rubbers. EUGENE GUTH, PAUL E. WACK, AND ROBERT L. ANTHONY 1137
Crystallization of Unvulcanized Rubber at Different Temperatures. LAWRENCE A. WOOD AND NORMAN BEKKEDAHL 1145
Tackiness of GR-S and Other Elastomers. W. F. BUSSE, J. M. LAMBERT, AND R. B. VERDERY 1163
Stress-Time-Temperature Relations in Polysulfide Rubbers. M. D. STERN AND A. V. TOBOLSKY 1178

RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry by payment of the dues ($2.50 per year) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Anyone who is not a member of the American Chemical Society may become an Associate Member of the Division of Rubber Chemistry upon payment of $5.00 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at a subscription price of $5.00 per year.

To these charges of $2.50 and $5.00, respectively, per year, postage of $.20 per year must be added for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given RUBBER CHEMISTRY AND TECHNOLOGY.

REPORT OF CONFERENCE ON POSTWAR PREPARATION AND PACKING OF RUBBER *

LONDON ADVISORY COMMITTEE FOR RUBBER RESEARCH
(CEYLON AND MALAYA)

IMPERIAL INSTITUTE, SOUTH KENSINGTON, LONDON, ENGLAND

On the recovery of Malaya, rubber will at first probably be prepared by somewhat crude methods, depending on the equipment and other material available. Arrangements are under consideration in other quarters to deal with this position. It is essential, however, to look ahead to the time when estates can reorganize the technique of preparation and packing on a permanent basis. The Committee has, therefore, assumed responsibility for making enquiries with a view to advising estates as to whether the methods used in 1939 should be reëstablished or whether improvements are practicable. Some of the recommendations made in this report also apply to holdings of 100 acres and less.

In order that the advice should be as sound as possible, a Conference of representatives of rubber manufacturing and trade organizations in Great Britain was called and asked to formulate recommendations which would enable growers to prepare and pack the bulk of their product in the form and quality most suitable for use by the manufacturers. The Committee wishes to acknowledge the helpful coöperation, as members of the Conference, of F. D. Ascoli and representatives appointed by the Federation of British Rubber & Allied Manufacturers' Associations, the Research Association of British Rubber Manufacturers, the London Association of Public Wharfingers, Ltd., the Federation of London Public Wharfingers, Ltd., the Rubber Trade Association, the Rubber Growers' Association, the United Warehouse Keepers' Conference, and rubber machinery manufacturers (Francis Shaw & Co., Ltd., and David Bridge & Co., Ltd.).

The Conference agreed that it was necessary to obtain the views of as many manufacturers as possible, both in this country and in the United States of America. The approach to manufacturers was made through the Rubber Manufacturers' Association of New York, the Federation of British Rubber & Allied Manufacturers' Associations, and the Research Association of British Rubber Manufacturers, all of whom took considerable pains to obtain detailed views from their members. The Conference is particularly indebted to A. L. Viles (President of the Rubber Manufacturers' Association of New York), E. J. Coles and S. D. Sutton (Federation of British Rubber & Allied Manufacturers' Associations) and B. J. Eaton (Research Association of British Rubber Manufacturers), who supervised the arrangements for the collection of information by the respective organizations with which they are connected.

* An abridgment of the original report, dated July 1945. Sections of the report which discuss in detail the subject of large central factories, a Minority Report, and an Appendix on the Large Scale Manufacture of Standard Smoked Sheet Rubber are omitted. The Conference, with P. J. Burgess as Chairman, comprised forty-three members.

VIEWS OF MANUFACTURERS

A summary of the views expressed by manufacturers is given in the form of a table which is self-explanatory.

TYPES OF RUBBER

Most manufacturers agree that the main product from estates should continue to consist of ribbed smoked sheet. Manufacturers are used to this type, and a generation of commercial and technical practices has been developed around it. Manufacturers on the whole are not prepared, under present circumstances, to take the initiative in suggesting sweeping changes. Any future improvements in methods of preparation must, therefore, be initiated by the producer, who cannot afford to remain complacently content in a competitive world of changing technical values.

The Conference has discussed the preparation of alternative forms and types offering theoretical advantages, but has come to the conclusion that definite recommendations must be deferred until they have been thoroughly tested and approved by manufacturers. The more important of these suggestions are discussed later in this report. For the present, estates are advised to concentrate on producing smoked sheet of the best quality as their main product. The Conference does not wish to suggest, however, that this form of rubber will necessarily remain the best for general purposes, since alternative forms may be evolved in due time which are superior to it. (*See* part entitled "Alternatives to smoked sheet for main products").

QUALITY OF SMOKED SHEET

During the initial period of reöccupation of Malaya, when adequate facilities may not be available for producing smoked sheet of the best quality, priority must be given to volume of output, followed as rapidly as possible by efforts to improve quality. Even if the preparation of smoked sheet is only a temporary phase, this form represents, for the time being, the main alternative to synthetics, and estates should therefore aim at producing a quality which will give the maximum satisfaction to manufacturers. To safeguard the interests of producers, the Conference suggests that, during this initial period, all rubber should be labelled "Emergency rubber". It is suggested also that grading should follow the simplified lines inaugurated as a war measure by the Ministry of Supply, and at present in use for shipments from Ceylon, *viz.*, three types of ribbed smoked sheet and four of crepe.

Most manufacturers consider that the best quality of smoked sheet is represented by the New York grade R.M.A. 1X, for which the specification lays emphasis on cleanness, appearance and absence of mould.

Manufacturers agree that the super-cleanness of 1X is not essential for all purposes, but is always an advantage. There is, however, little difference in the cost of preparing clean as against dirty rubber, and it is uneconomical for estates not to produce the highest possible percentage of their crop as clean as 1X. The discount for dirty rubber may be one-eighth of a penny per pound or even more, which would easily cover the cost of the extra care required to produce clean rubber. All estates strain latex as a matter of course. Keeping the factory scrupulously clean is not expensive. It is also important to allow the bulked diluted latex to settle so as to separate particles of sand which accidentally contaminate the latex in the field and are in many cases sufficiently

fine to pass through the strainer. The improvement in cleanness may not be obvious on inspection, because grains of sand in rubber, unlike specks of bark, are generally invisible, but the improvement is real and the cleanness of plantation rubber is an important item in determining the attitude of manufacturers, particularly as synthetics are not liable to the same contamination.

Apart from cleanness and general appearance, the other main factor in determining quality as defined by the specification for 1X is the group of defects comprising mould, rust and bubbles. These defects receive much prominence in the grading specification, but are not usually considered by technologists to be harmful. If this view is correct, endeavors should be made to have the classifications altered. More precise information is required, however, and the London Advisory Committee should obtain this information from the appropriate manufacturers' associations, *i.e.*, The Rubber Manufacturers' Association of New York, The Federation of British Rubber & Allied Manufacturers' Associations, and the Research Association of British Rubber Manufacturers.

Estates which are successful in marketing a substantial portion of their rubber as 1X are generally satisfied that the quality of their rubber is beyond reproach. It should be appreciated, however, that grade 1X may sometimes have abnormal processing and vulcanizing properties and, although such abnormalities are not likely to have an immediate effect on the demand for the rubber of the estates concerned, they are likely, in the long run, to prejudice the market for natural rubber in relation to that for synthetics. These abnormalities cannot be detected by visual inspection and are revealed only when the rubber is tested or, more commonly, when it is in process of manufacture into finished articles. Among the causes of abnormalities are departure from the recommended methods of preparation and inherent variation in latices. The producers' research organizations have laid down conditions which should be observed in the preparation of smoked sheet, and estates are urged to study them carefully and not to depart from them without technical advice. They are also advised to bulk their latex on the largest scale possible so as to obtain uniform technical properties.

COST OF PRODUCTION

Attention is called to the importance of cheap production and to the probability that world-wide economic factors and local circumstances will increase costs beyond those of 1939. Under normal trading conditions price will be an important factor in determining the relative demands for natural and synthetic rubbers. At present each has technical advantages, which, for certain uses, are more important than price. New synthetics are continually being developed, however, and methods of polymerization are being improved so that natural rubber may lose the advantage of being essential for some purposes. The price factor will, therefore, increase in importance as the years pass.

Political and economic, as well as technical factors are involved in production costs, but the latter are the only ones which the Conference is entitled to discuss. Technical factors depend in part on local circumstances, and the Conference can do little more than call attention to the importance of an efficient economy.

The size of the latex crop relative to the cropped area and the tapping force offers the most scope for low level costs; this requires careful study on each estate. Processing costs are relatively small and can be kept low by installing mechanical equipment to save labor and fuel which may be more expensive in

SUMMARY OF VIEWS OF BRITISH AND AMERICAN MANUFACTURERS ON POSTWAR RUBBER

Subject	U.S.A. manufacturers	British Manufacturers		
		Members of R.A.B.R.M.	Tire Manufacturers' Conference	Manufacturers of mechanical goods (F.B.R.M.A.)
1. (a) Main product	R.S.S. 1X should continue as main product until something better is found.	R.S.S. should continue as main product.	Various grades required. There will remain a heavy demand for lower grades at appropriate prices.	First grade S.S. is most satisfactory form.
Suggested improvements	Try to improve uniformity. Large-scale bulking is a step in the right direction. A continuous process is also desirable if it does not increase cost. The effect of maturation requires further study. Some manufacturers have noticed high physical properties in R.S.S. 4 and 5, probably due to maturation. Latex is specially treated in Indo-China to achieve this effect for one important manufacturer.	Bulk of manufacturers consider that an improvement in uniformity is desirable, but several are satisfied.	Main requirements are uniformity of cure, cleanness and high plasticity (easy milling). Need for improved uniformity in each grade. Doubts expressed whether central factories would be advantageous from all angles. Would welcome further information.	Large-scale bulking and continuous process both favored. Care required in collection to use a preservative which has no adverse effect on manufactured articles. Control of smoking process is also important in the interests of uniformity.
(c) Cleanness	Superlatively clean rubber is not essential for majority of uses, but cleanness as represented by R.S.S. 1X is not a disadvantage, whatever the product.	A few firms stress the importance of cleanness.	There is need for greater cleanness.	Superlatively clean rubber is not essential for all manufactured articles, but a minimum standard of cleanness should be maintained. Superlatively clean rubber should be available for some purposes.
2. (a) Pale crepe	A small percentage of total production is required for light colored articles and medical goods. R.M.A. 1X is the best product.	Required for bright colored articles and food containers.	—	Favored for colored articles.
(b) Suggested improvements	Try to produce light colored sheet at lower cost than crepe. Physical properties of air-dried sheet are not at present satisfactory.	—	—	Add an ingredient to latex to prevent development of pink color on storing.
3. Brown crepe	—	Used for cheapness and where soft rubber is required.	—	Satisfactory.

		where soft rubber is required.	—	Satisfactory.

SUMMARY OF VIEWS OF BRITISH AND AMERICAN MANUFACTURERS ON PREPARATION AND PACKING

Subject	U.S.A. manufacturers	British Manufacturers		
		Members of R.A.B.R.M.	Tire Manufacturers' Conference	Manufacturers of mechanical goods (F.B.R.M.A.)
4. Specialties	Consideration should be given to low water absorption, peptized, U.S.F. and sprayed rubber. A small demand is expected for these types. Experience is too limited to indicate whether the demand for any of them is likely to reach large proportions.	Interest displayed in peptized rubber, purified rubber, dark grade of sheet, powdered and pellet rubber.	Need for new and improved grades with new characteristics.	A few manufacturers are interested in uniform peptized rubber. Powdered rubber may be useful in the manufacture of solution. One manufacturer refers to the advantage of pellet rubber.
5. Packaging	Bulk opinion favors "bare-back" packing for R.S.S. "Bare-back" packing is unsuitable where dock inspection is required. It is also unsuitable for crepe on account of color. The introduction of smaller packages should be left to experimentation. New type of container which will not adhere to or contaminate rubber is required.	Many firms dissatisfied with present packages, but express different views on possible improvements. A few firms favor smaller packages.	A 100-lb. unit would be convenient.	Wooden cases preferable, but contamination of rubber by splinters is a difficulty. One manufacturer strongly prefers "bare-back" bales on account of cleanness. Another would like the strengthening frame outside instead of inside wooden cases so that rubber can be removed easily. Some favor smaller packages. Others suggest slabs 3 inches thick within bales, or packing in well talced layers up to 1 inch thick. Several refer to the advantages of zinc stearate as a dusting powder.
6. Grading	—	A few firms express interest in stabilized prices and (or) in modification of specification.	—	According to one firm, preparation and grading should be controlled by specifications drawn up by British and American manufacturers.
7. Liquid latex	Wide expansion in the demand for preserved latex is expected.	—	—	—

the post-war era. Sheeting batteries designed to secure the utmost economy in power and labor, and smoke houses which facilitate handling and reduce fuel consumption are obviously of importance. Materials and labor employed in packing also offer scope for small economies. It should be remembered, however, that changes in processing are liable to be costly.

PACKING

Manufacturers are generally critical of the way rubber is packed, and are equally critical of each other's suggested remedies. Wooden cases give rise to splinters. Hessian, unless the greatest care is given to surface treatment, is liable to contaminate rubber like jute fibre, and it sometimes sticks badly. All manufacturers dislike metal bands around the rubber because they often penetrate into the bales and are difficult to remove. Rubber packed in hessian, as also smoked sheet packed without bands and completely wrapped in rubber of equal quality with no outside case of hessian ("bare-back"), is liable to become misshapen, and cannot be neatly piled in warehouses.

To find a packing material which will satisfy all the requirements of non-adhesion, prevention of splinters, dirt, etc., will no doubt be possible, but may be expensive and, therefore, not feasible for ordinary shipments. It is evident that the study of packing methods and materials should receive priority in the immediate postwar period.

American manufacturers offer a guide to postwar policy by stating that, before the outbreak of war, "bare-back" had a very favorable reception, and it is not unreasonable to assume that shipment in this form will gain in favor as time goes on. There will undoubtedly be a demand, however, for both cased and baled rubber from certain manufacturers all over the world, and estates will expect a premium to cover the cost of any special packing.

In view of the fact that some manufacturers have expressed a desire for smaller packages and of the fact also that GR-S (the chief American type of synthetic rubber) is packed in small containers, consideration was given to the problem of shipping rubber in smaller packages. The Conference considered a proposal for the reduction in the weight of packages of baled rubber. An important consideration appears to be the attitude of the shipping companies, since the proposal may involve the assessment of freight on weight instead of on measurement. The Conference recognizes the advantage of smaller packages in handling and considers that trial shipments should be made, as suggested by American manufacturers, to ascertain what increase in costs is involved.

Rubber packed in cases should continue to be packed in cases of five cubic feet.

ALTERNATIVES TO SMOKED SHEET FOR MAIN PRODUCT

FERMENTED RUBBER

The Conference has been impressed by the views of some manufacturers who consider that some lower grades have better physical properties than 1X for the reason that the rubber has been allowed to ferment. It is also of interest that an important European manufacturer has for some time made large and regular purchases of fermented rubber containing more serum substances than usual. If it can be confirmed, and manufacturers agree, that fermented rubber is superior to 1X, there should be no great difficulty in developing a

process which is not more expensive than that employed in the preparation of 1X sheet. If it is found desirable to include more of the naturally occurring serum substances, the cost of fermented rubber, according to present information, should be cheaper than that of standard smoked sheet. The first step would be to obtain as quickly as possible the required technical information regarding the merits of fermentation and extra serum substances.

Fermented rubber from "matured slab" was first prepared and examined many years ago by Eaton in Malaya. Promising results were obtained, but manufacturers at that time did not appear to be greatly impressed by its practical advantages. Testing methods have now improved, and a further study of the subject along thoroughly practical lines should determine why some manufacturers prefer fermented rubber. It will still be necessary to aim at producing fermented rubber in strip or sheet form to facilitate drying, to dry in smoke for keeping properties, and to pay strict attention to cleanness. The appearance will be less attractive than that of 1X smoked sheet, but, with the coöperation of the commercial interests concerned, there should be no difficulty in marketing it as a special grade commanding a price in accordance with its technical merits.

SPRAYED RUBBER

A spray-drying process requires expensive plant and would only be suitable for large-scale operations. Information supplied by a British manufacturer of spray-drying plant indicates that the equipment and operating costs would be higher than for smoked sheet. The inclusion of all the serum substances would, however, result in a higher output which might compensate for the extra cost. In the past, spray-dried rubber was too hard for most manufacturers, but new methods of softening rubber have now been evolved and might be successfully applied to the spray-drying process. Manufacturers have not so far expressed objection to the principle of diluting the rubber hydrocarbon with naturally occurring serum substances, and the spray-drying process is worthy of further study.

CONTINUOUS STRIP RUBBER

The Conference has also given attention to the desirability of producing rubber in the form of a continuous strip. Such a process might save labor and result in a more uniform product, but might require extra coagulant for quick coagulation. If the strip is to be dried rapidly and continuously, more fuel might be required than for smoked sheet. Further information is desirable.

SPECIALITIES

The quality of sheet from small holdings is adequate for many purposes and, to reap the full benefit of enterprise and technical efficiency, it is desirable that estates should develop new types of rubber for special purposes. Possible developments are detailed below. There is a large potential demand for some of them.

A few of the larger organizations in Malaya were already studying some of these possibilities at the beginning of the War. The average European estate is, however, too small to take the initiative in developing new markets, and some of the more promising lines are doomed to failure if they are produced by a large number of average estates, working independently. The development of new types is more likely to be successful if undertaken by large organizations.

SOFTENED RUBBER

Rubber softened by "peptization" is obtained by adding to latex a small quantity of an ingredient (possibly a patented proprietary product) which makes the rubber very soft when dry. The rubber is of good quality, and has the advantage that it can be easily manipulated by manufacturers. The potential demand is large. The softness of the rubber would have to be controlled.

RUBBER-CARBON BLACK MIXTURES

Large quantities of "rubber-carbon black" mixtures are used by manufacturers. Carbon black is very troublesome to mix with dry rubber and much labor would be saved if it were first mixed with latex and the rubber then coagulated, sheeted and dried. The process is very attractive and is being used in the case of synthetic latices, which are manufactured near the source of carbon black and have a particle size much smaller than that of natural latex. In the case of natural latex, it would be necessary to import the carbon black and then reëxport it mixed in with the rubber. Carbon black in the form of beads is usually shipped in cases holding six 50-lb bags, a case occupying about twice the bulk of the same weight of smoked sheet.

There are many grades of carbon black, and standardization would be essential. There is also a wide range of possible proportions, the most suitable probably being of the order of 50 per cent by weight of the rubber.

FORMALDEHYDE RUBBER

The treatment of latex with formaldehyde under certain conditions has been claimed to produce a rubber with superior mechanical properties and of interest to tire manufacturers. The bulk of plantation rubber is used in the manufacture of tires, and any method of preparation which increases its value for this purpose is of corresponding importance, provided no increased cost is involved. The superior mechanical properties of formaldehyde rubber have not so far been investigated by independent workers, and the published description of the method of preparation suggests that the cost will be high, but the process is an indication of the possibility of preparing and marketing new types of rubber of special value for important manufacturers.

PURIFIED RUBBER

Interest is also displayed in specially purified or deproteinized rubber, but the potential demand is relatively small, since the rubber is advantageous mainly for purposes where electrical properties are of importance.

POWDERED RUBBER

Some manufacturers are interested in powdered rubber and others in rubber in the form of pellets, both of which offer advantages to them in regard to automatic weighing and handling. Such rubbers are not easy to prepare, and the problem of packing and storing without massing is a difficult one. Powdered rubber is bound to occupy greater bulk than sheet and so cost more in packing and transport. Powdered rubber is more easily prepared from latex containing large quantities of compounding ingredients, and such powder might form the basis of a new technique (injection moulding, for example) of rubber goods manufacture.

PALE SHEET

American manufacturers have called attention to the desirability of marketing sheet rubber of the same color as pale crepe but at a lower price. The preparation of such material should not offer insuperable difficulties, but air-dried sheet has so far been found to have disappointing keeping properties after vulcanization; drying in smoke has apparently unsuspected virtues worthy of still further investigation. The demand for pale sheet would depend on properties and price, but is never likely to exceed that for pale crepe, which is now used almost wholly for bright colored articles, food packages and surgical goods, etc.

SOLE CREPE

This type of crepe is not of great interest to rubber manufacturers and is, therefore, outside the range of products considered by the Conference, which has no representative from the boot and shoe trade.

PRESERVED LATEX

Most manufacturers do not use and are not likely to use preserved latex for their main requirements, as some essential mechanical properties can only be obtained by mechanical working of dry mixtures. Preserved latex can be used only for special purposes. The popularity of some of these purposes was, however, becoming increasingly noticeable before the War, and in 1940 the export of rubber in the form of latex exceeded 3 percent of the dry product. The potential expansion in the use of preserved latex after the War is very large, and is considered to be promising.

The preparation of preserved latex, although simple in principle, requires careful attention to detail. The requirements of manufacturers are likely to become more exacting, and only estates able to make special arrangements for the disposal of their product are advised to treat the bulk of their output in liquid form. In any circumstances, some form of concentration will be necessary to avoid excessive cost of packing and freight for excess water. It is also probable that for economy in transport, bulk shipments in steamer tanks will become an important issue. This involves considerable equipment which could not be operated economically by small independent units. Producers near a port of shipment have advantages over those further inland.

CONCLUSIONS

Smoked sheet must continue to be the main product for the time being. Pale crepe and off grades are also likely to be required in prewar proportions.

There are good prospects of an important increase in the demand for concentrated latex. Much of this demand represents an additional consumption of rubber, and is not at the expense of smoked sheet and crepe. Large organizations, particularly those near a port of shipment, are in a stronger position to meet latex requirements than are small organizations.

All rubber exported from Malaya should, for a period, be marked "Emergency rubber".

The simplified system of grading smoked sheet and pale crepe introduced by the Ministry of Supply as a war measure should be continued (three types of smoked sheet and four of crepe).

The London Advisory Committee for Rubber Research (Ceylon and Malaya) is recommended to obtain as much information as possible about the technical effects of the group of defects comprised under mould, bubbles and rust, and to communicate the results of their findings to the Rubber Trade Association if a change in the grading specifications is considered desirable.

Methods of packing rubber are, on the whole, unsatisfactory and require further study.

There is likely to be an increase in the popularity of "bare-back" bales, which consist of rubber pocked in outside wrapper sheets of the same quality, without metal bands or hessian covering.

The Conference recognizes the advantages of smaller packages in handling and recommends that trial shipments should be made to ascertain what increase in cost is involved.

The Conference has considered alternatives to smoked sheet as the main product. Fermented rubber, spray-dried latex and rubber produced by a continuous process are all promising in some directions. Their preparation and utilization should be studied at the earliest opportunity. A fair amount of information is already available about some of them, but there are important gaps which must be filled in before any recommendations can be made.

The development of special types of rubber for specific manufacturing purposes is of considerable importance. These are best studied and developed by a central research organization in association with some of the larger groups of estates. The following is a list of the specialties discussed by the conference:

(1) Rubber softened by "peptization"
(2) Rubber-carbon black mixtures
(3) Purified or deproteinized rubber
(4) Rubber powder
(5) Pale sheet equivalent to pale crepe
(6) Formaldehyde rubber

The Conference has carefully considered the advantages and disadvantages of preparing, grading and packing rubber in large central factories. The conclusion has been reached that such factories are not likely to be as economical as smaller units which serve individual estates. Some members of the Conference consider that increase in cost would be trivial, but others are of the opinion that the all-in costs are bound to be considerably higher than those of smaller units.

Large factories will at the outset also have to contend with a number of difficulties inherent in large scale operations, *e.g.*, delayed coagulation.

Owing to the existing location of estates and the configuration of the land, some of the members of the Conference consider that large central factories would be impractical over a great part of Malaya. On the other hand, it is expected that central factories would be able to market a technically more uniform product than a corresponding number of individual units.

Large central factories may have potentialities, but as there is a divergence of views, convincing proof can come only from an actual "try-out", which could not be undertaken immediately following the reöccupation of Malaya without delaying the production of rubber.

The Conference has carefully considered the advantages and disadvantages of processing, grading and packing rubber in large size central factories. The conclusion has been reached that such factories are not likely to be as economical as smaller units serving individual estates.

Large factories will also have to contend with a number of difficulties inherent to large scale operations in Eastern countries.

Large factories might be able to market a technically more uniform product than a corresponding number of individual units, but this does not necessarily follow.

A point that should not to be overlooked when considering the transportation of latex over long distances is that two-thirds of the weight so carried is water.

Owing to the existing location of estates and the configuration of the land, it is very doubtful whether large central factories would be practicable over a large portion of Malaya.

INFLUENCE OF VULCANIZATION ON THE OXIDIZABILITY OF RUBBER

II. VULCANIZING AGENTS OTHER THAN SULFUR *

JEAN LE BRAS

INSTITUT FRANÇAIS DU CAOUTCHOUC, PARIS, FRANCE

INTRODUCTION

In 1937 Dufraisse and Étienne[1] published a systematic study of the influence of vulcanization on the oxidizability of rubber. The authors dealt with the various methods of vulcanizing with sulfur, including elemental sulfur, nascent sulfur (the Peachey process and tetramethylthiuram disulfide), and sulfur monochloride, and they proved convincingly that, as a general principle, rubber increases in oxidizability with increase in the percentage of combined sulfur. As a result of other experiments later, Kemp and his collaborators[2] were led to similar conclusions.

The experiments of Dufraisse and Étienne covered an extremely wide field of vulcanization, and make it possible to draw two particularly interesting conclusions. First, beyond a definite limiting upper range, sulfur becomes progressively less harmful, as a consequence of which the oxidizability tends toward a plateau and in some cases even passes through a maximum. However, this latter phenomenon may be attributed to a decrease in the permeability to oxygen. Secondly, with low percentages of sulfur, a minimum oxidizability is observed, and this agent therefore appears to behave as a protective agent, a phenomenon which seems to conform to more recent observations of Stevens and Gaunt[3] and of Blake and Bruce[4], whose investigations point to the antioxygenic effect of small quantities of sulfur.

It seemed of interest to complete this preliminary and exploratory work by studying the effects of vulcanization with agents other than sulfur on the oxidizability of the products. Dufraisse and Le Bras[5] have already studied vulcanization by nitro compounds and by peroxides, choosing as typical of these types *m*-dinitrobenzene, trinitrobenzene, and benzoyl peroxide. Their experiments showed that, as with sulfur, the oxidizability increased with increase in the percentage of vulcanizing agent combined with the rubber, and tended toward a plateau. On the other hand, these agents did not, at least in small percentages, seem to play the antioxygenic role manifested by sulfur.

In the present work, the effects of still other vulcanizing agents were studied by determining, as was done in the previous investigation, the influence of the time of vulcanization and of the proportion of vulcanizing agent.

The method employed was the manometric method[6]. The rapidity with which results can be obtained, and the small volume of sample which is necessary have made its use of particular advantage, for in some cases relatively

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 18, No. 9, pages 289–302, November 1941. This paper was presented at the Rubber Congress held in Paris, May 1940. Part I of this work entitled "The Influence of Vulcanization on Oxidizability in Relation to Aging", by Dufraisse and Étienne, was published in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 11, No. 2, pages 282–309, April 1938.

rare compounds have been tested in the vulcanizates. On the other hand, the correlation which has been established between manometric measurements and aging in the Geer oven[7] of various types of mixtures vulcanized with sulfur makes it justifiable to assume, until there is proof to the contrary, that the results obtained with the vulcanizates studied in the present work are a fairly trustworthy indication of what their aging characteristics would be.

The vulcanizing agents studied in the present work included selenium and representatives of types of compounds whose vulcanizing power has been recognized only more or less recently. It was believed that a study of these new agents, of which the present paper is but a small part, would be a step toward an exact interpretation of the mechanism of vulcanization, particularly if advantage were to be taken of the wholly new method of vulcanization described by Dufraisse and Compagnon[8]. There is every reason to believe that comparisons between these different processes and the correlative effects likely to be found will give information which will be more fruitful than any obtained by experiments with mixtures vulcanized with sulfur, in spite of the considerable amount of work which has already been expended in this latter field.

Before describing the results of the present investigation, it seems appropriate to survey briefly what has been done in this little studied field of rubber chemistry.

HISTORICAL

To Boggs[9], whose untimely death deprived the American rubber industry of one of its most eminent technologists, is due the first use of selenium as a vulcanizing agent. There had unquestionably been various suggestions regarding the possibility of using this agent, but it was only with the aid of certain organic accelerators that Boggs succeeded in actually vulcanizing rubber samples. Among the accelerators which were particularly effective, he cited *p*-nitrosodimethylaniline and piperidinium pentamethylenedithiocarbamate. However, the times of cure were still very slow, and it is chiefly as a secondary vulcanizing agent with sulfur that selenium has been found to be useful.

If we limit ourselves to the aging properties and oxidizability of such vulcanizates, only scant information is to be found in the literature. Some tests carried out by Boggs and Follansbee[10] and by the R. T. Vanderbilt Company[11] indicate that selenium behaves almost like sulfur. However, the increased resistance to aging described in the work of the R. T. Vanderbilt Company seems to be a result merely of undercuring.

The vulcanizing power of diazoaminobenzene was discovered by Buizov[10] in 1921. However, Buizov himself did not attach any great significance to this discovery, and only recently have Fisher[13] and Levi[14] drawn the attention of rubber chemists and technologists to this compound and its derivatives. These compounds vulcanize rubber without requiring the presence of any other substance. During the heating process, gas is evolved, probably nitrogen, and this sometimes results in porous vulcanizates.

According to Levi[14], the vulcanizates age badly and become sticky; on the contrary, Fisher[15] later found that some of these vulcanizates have good aging properties, particularly when the vulcanizing agent is a derivative of diazoaminobenzene, *e.g.*, *N*-benzyldiazoaminobenzene, which acts at the same time as an antioxygenic agent. However, no systematic study of their oxidizability has been undertaken up to the present time.

Fisher, whose work has been mentioned above, carried out some remarkable investigations of vulcanization without sulfur. In 1933 he discovered the vul-

canizing power of halogenated quinones[16], some of which are capable alone of bringing about vulcanization, others of which require the presence of oxidizing agents, such as lead peroxide, manganese dioxide, and mercuric oxide. In a patent of 1936[13], Fisher cites, among other compounds, the use of quinone oximes, quinone imines and quinone haloimines. This vulcanizing action was likewise pointed out by Spence and Ferry[17], who found that the polymerization of rubber is increased by the addition to latex of various quinones and their halogenated or imino derivatives.

Fisher showed that most of these agents have good antioxygenic power. He carried out some experiments in which a small percentage, *i.e.*, the amount of antioxygenic substance ordinarily added, of some of these compounds was added to an ordinary rubber mixture containing sulfur. In this way he proved that all three of the compounds which he tested, *viz.*, *p*-quinone monoanil, *p*-quinone dianil and *p*-quinone-bis-β-naphthylimine, improved aging very markedly.

Finally, among the vulcanizates whose oxidation was studied in the present work, are some which are formed by the action of an aromatic amine and an oxidizing agent. Here again it was Fisher who has called attention to these compounds. He called these agents "leuco bases of quinone imines", *i.e.*, compounds which are capable of being transformed by oxidation into quinone imines, and can be used for preparing these latter compounds within the rubber mixture itself by the action of a suitable oxidizing agent.

Fisher asserts, without however offering any experimental data in support that the use of an oxidizing agent with these various chemical compounds imparts improved aging properties to the vulcanizates, and he observed that this appears to be at variance with the generally accepted principles of the preservation of rubber. It will be seen in what follows that these facts agree with the results of the systematic experiments which have been carried out in the present work.

All measurements of the oxidizability which are to be described were carried out in darkness in oxygen at 80° C.

SELENIUM

SELENIUM ALONE

It was necessary first of all to determine the influence of selenium on the oxidizability of mixtures prepared with this element alone as vulcanizing agent. As a base mixture, a relatively simple formulation used by Blake[18] was chosen:

Smoked sheet	100
Selenium	125
p-Nitrosodimethylaniline	3
Zinc oxide	5

This was heated for different times at 143° C. Other mixtures contained different proportions of selenium. Table 1 gives the compositions and the vulcanizing conditions of the various samples.

No systematic measurements were made either of the mechanical properties of the vulcanizates nor of the vulcanizates prepared in the other series of experiments of the present work. In a study of this character, it is sufficient to judge the samples according to their appearance and feeling in order to obtain a general idea of their state of vulcanization.

In the first series, VA_1 had reached a state where it was well set; VA_2 and VA_3 were still very sluggish; VA_4 and VA_5 were well cured. In the second

TABLE 1

Variation in time of vulcanization			Variation in proportion of selenium		
Mixture	Parts of selenium per 100 parts of rubber	Hours of at 143° C	Mixture	Parts of selenium per 100 parts of rubber	Hours of at 143° C
VA_1	125	1	VB_1	10	8
VA_2	125	3	BB_2	30	8
VA_3	125	5	VB_3	60	8
VA_4	125	8	VB_4	125	8
VA_5	125	16	VB_5	250	8

series, VB_1 and VB_2 were very soft and filled with bubbles; VB_3 was still soft; VB_4 was well cured; VB_5 was a little hard and sluggish.

Influence of the time of vulcanization (VA series).—Figure 1 shows the oxidation curves of the five mixtures of the VA series, as well as the curves of a mixture VA_0 of the same composition which had not been heated, and of smoked-sheet rubber FF alone, milled for the same time as the other samples.

The oxidizability measurements were made at 80° C on amounts of the mixtures corresponding to 1 gram of actual rubber.

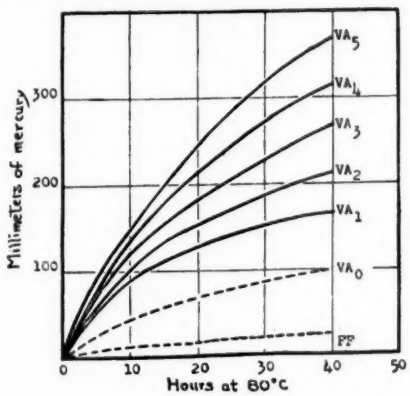


FIG. 1.—Influence of time of vulcanization at 143° C on the oxidizability at 80° C of selenium mixtures. VA_0 is the raw mixture. FF is smoked sheet alone.

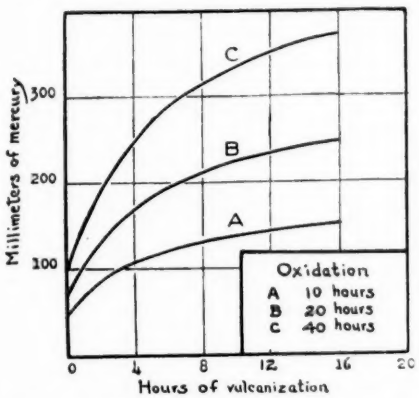


FIG. 1a.—Oxidizability at 80° C as a function of the time of vulcanization at 143° C of selenium mixtures of the VA series.

It is quite evident that the oxidizability increases with increase in the time of vulcanization, but it is not proportional to the time, and the relation can be seen more clearly by plotting as a function of the time of vulcanization the oxidation values taken from the family of curves in Figure 1 for oxidation times of 10, 20 and 40 hours. Figure 1a shows the curves obtained in this way. The curves flatten more and more and each tends toward a plateau.

The course of these curves corresponds perfectly to the results obtained by Blake[18] in the determination of combined selenium. Blake showed in

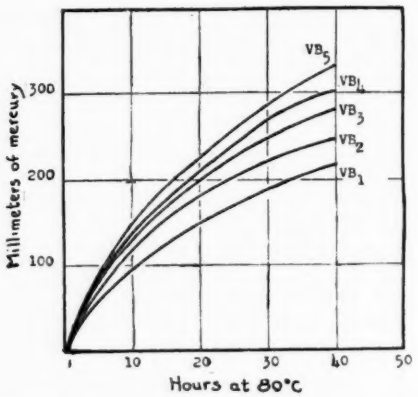


FIG. 2.—Influence of the percentage of selenium on the oxidizability at 80° C of selenium mixtures.

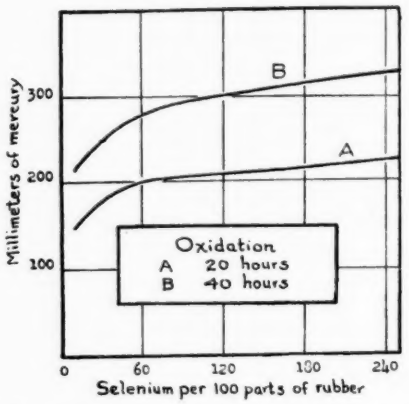


FIG. 2a.—Oxidizability at 80° C as a function of the percentage of selenium in mixtures of the VB series.

effect that, for a mixture of the same composition as that used in the present work, the percentage of combined selenium increases at first rapidly with the time of vulcanization, then progressively less rapidly, so that the reaction can be regarded as practically complete at the end of a heating period of 8 hours.

It is reasonable, therefore, to assume that the oxidizability increases with with increase in the percentage of combined selenium, *i.e.*, with the degree of vulcanization. Accordingly the same phenomenon is found as has been ob-

served in the case of sulfur. However, as is known, vulcanization by selenium is much less far advanced than with sulfur, and this may explain why with selenium there is no maximum oxidizability.

Influence of the percentage of selenium (VB series).—Figure 2 shows oxidation curves of the five mixtures of the VB series. The results agree well with what might be expected in view of the similarity with sulfur observed in the previous series of experiments.

The oxidizability increases with increase in the percentage of selenium in the mixture and probably, as a consequence, with the percentage of combined selenium. The curves in Figure 2b show plainly that here too this oxidizability tends toward a maximum.

It must therefore be concluded that, in general, selenium behaves exactly like sulfur from the standpoint of oxidizability. It still remains, however, to determine whether, with small percentages of selenium, there is, as with sulfur, a minimum point of oxidizability. This is a question which it is hoped that it will be possible to answer later.

SELENIUM AND SULFUR

After having determined the influence on oxidizability of vulcanization by selenium alone, it was of interest to examine the behavior of mixtures containing both sulfur and selenium.

To this end samples SA, SB, and SC were prepared from a mixture chosen from the work of Boggs and Follansbee[10].

Smoked sheet	100
Ethylideneaniline	0.75
Diphenylguanidine	0.75
Zinc oxide	17
Selenium	variable
Sulfur	variable

The percentages of sulfur and of selenium added and the times of vulcanization are given in Table 2.

This makes three series of samples, vulcanized under the same conditions, and containing, respectively: (1) 4 parts of sulfur; (2) 4 parts of sulfur and 2.5

TABLE 2

Mixture	Sulfur (parts per 100 parts of rubber)	Selenium (parts per 100 parts of rubber)	Minutes of vulcanization at 143° C
SA_1	4	0	20
SA_2	4	0	40
SA_3	4	0	60
SA_4	4	0	90
SA_5	4	0	120
SB_1	4	2.5	20
SB_2	4	2.5	40
SB_3	4	2.5	60
SB_4	4	2.5	90
SB_5	4	2.5	120
SC_1	6.5	0	20
SC_2	6.5	0	40
SC_3	6.5	0	60
SC_4	6.5	0	90
SC_5	6.5	0	120

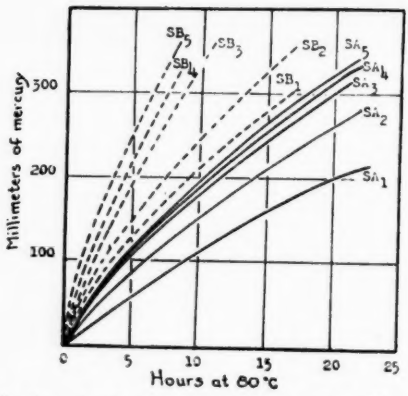


FIG. 3.—Influence of the time of vulcanization at 143° C on the oxidizability at 80° C of mixtures containing selenium and sulfur.

SA series—4 parts of sulfur
SB series—4 parts of sulfur and 2.5 parts of selenium

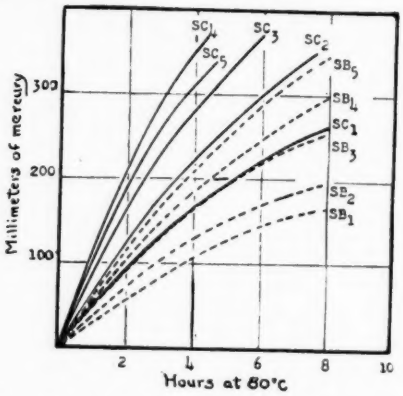


FIG. 3a.—Influence of time of vulcanization at 143° C on the oxidizability at 80° C of mixtures containing selenium and sulfur.

SC series—6.5 parts of sulfur
SB series—4 parts of sulfur and 2.5 parts of selenium

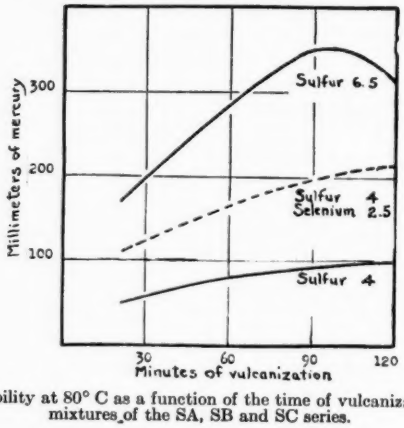


FIG. 3b.—Oxidizability at 80° C as a function of the time of vulcanization at 143° C of mixtures of the SA, SB and SC series.

parts of selenium, and (3) 6.5 parts of sulfur. All the samples were well vulcanized, and did not show any marked differences in appearance, except that SA_1 was a little soft, and SC_5 was slightly harder than the others.

The measurements of oxidizability, carried out at 80° C, gave the results shown graphically in Figures 3 and 3a. For greater clarity, two graphs are included, on each of which the oxidation curves of the sulfur-selenium mixtures are shown.

The results show: (1) that the addition of 2.5 parts of selenium makes the mixtures oxidize more rapidly, and (2) the replacement of this selenium by sulfur increases the oxidizability still more.

This last point is explained quite easily by the fact that selenium is a less powerful vulcanizing agent than sulfur; hence, in every case it is the degree of vulcanization of a mixture which governs its oxidizability.

Figure 3b shows these results graphically in a more convincing way. It is evidence that the mixture containing 6.5 parts of sulfur shows, at sufficiently long times of vulcanization, the maximum oxidizability observed by Dufraisse and Étienne with similar mixtures.

These results are in harmony with those reported earlier by the R. T. Vanderbilt Company[11]. According to their results, undervulcanized mixtures seem to improve in quality after four days of aging in the oxygen bomb because, from the point of view of mechanical properties, overvulcanization outweighs the deterioration which results from oxidation. On the other hand when vulcanization is sufficiently advanced, the loss in tensile strength is practically the same for mixtures vulcanized with sulfur alone as for those vulcanized with sulfur and selenium.

The combined use of these two vulcanizing agents certainly makes it possible to improve the physical properties of the vulcanizates, but from the point of view of oxidizability alone, the effects of selenium must be regarded as strictly comparable with those of sulfur.

DIAZOAMINOBENZENE

The mixture which was studied was composed simply of smoked-sheet rubber and diazoaminobenzene. Since this method of vulcanizing rubber is so little known, it may be of interest to describe in some detail the products obtained.

When a mixture of 100 parts of smoked sheet and 5 parts of diazoaminobenzene is heated for 1 or 2 minutes at 143° C, products are obtained which are barely set, and are sticky and filled with large bubbles. When the mixture is heated for three or four minutes, it commences to show the characteristics of vulcanized rubber, but it still contains many bubbles. When heated still longer, the mixture becomes well vulcanized and there is a resorption of the bubbles until, by heating for periods longer than 30 minutes, they become almost inappreciable.

Diazoaminobenzene gives a remarkably extended plateau effect, and vulcanization can be continued from 10 minutes to 8 hours without any appreciable change in the mechanical properties of the vulcanizates. This is not the place to enter into a discussion of the mode of action of diazoaminobenzene, but it is probable that nitrogen is liberated and various products such as diphenylamine, aminobiphenyl and perhaps the corresponding azo derivate are formed.

Table 3 shows the compositions and cures of the various mixtures which were prepared.

TABLE 3

Time of vulcanization of a mixture of 100 parts of rubber and 5 parts of diazoaminobenzene		Parts of diazoaminobenzene per 100 parts of rubber in mixtures vulcanized for 40 minutes at 143° C	
Mixture	Minutes at 143° C	Mixture	Diazoaminobenzene
DA_1	5	DB_1	1
DA_2	10	DB_2	3
DA_3	20	DB_3	5
DA_4	30	DB_4	7
DA_5	40	DB_5	10
DA_6	60	DB_6	15
DA_7	120	DB_7	20
DA_8	240	—	—
DA_9	480		

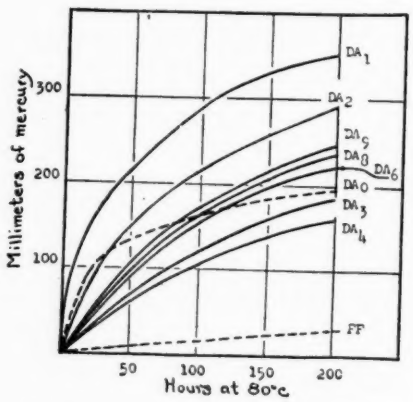


FIG. 4.—Influence of time of vulcanization at 143° C on the oxidizability at 80° C of diazoaminobenzene mixtures.

DA_0 is the raw mixture
FF is smoked sheet alone

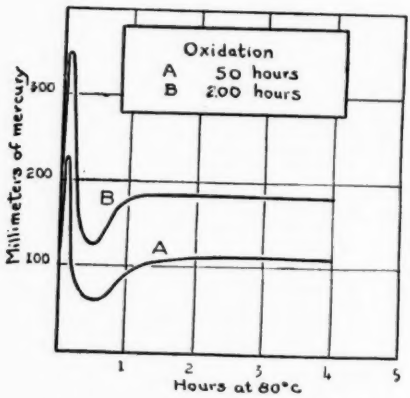


FIG. 4a.—Oxidizability at 80° C as a function of the time of vulcanization at 143° C of diazoaminobenzene mixtures of the DA series.

The products obtained from the mixtures of DA series did not show any significant differences in quality. In the DB series, DB_1 was porous and barely set; the others were well vulcanized, in fact DB_6 and DB_7 tended to be fragile and their fractured surfaces were lustrous.

Influence of the time of vulcanization (*DA series*).—Figures 4 and 4a show the oxidizability of the vulcanizates as a function of the time of vulcanization. A short heating period gave products which were extremely oxidizable, but with increase in the time of heating the oxidizability decreased rapidly, passed through a minimum at about 30 minutes' vulcanization, then increased a little and remained practically constant even for long periods of vulcanization.

In Figure 4 the curve represented as a broken line shows the oxidation of the unvulcanized mixture DA_0. From the position of this curve in relation to the curve of smoked sheet alone (FF), it might seem, at first thought, that diazoaminobenzene has considerable proöxygenic power. In reality, however, the vulcanizing power of this compound is so great that, by the effect of heating at 80° C, it brings about a state of vulcanization whereby the oxidizability is increased.

Oxidation measurements of samples vulcanized for 1, 2, 3 and 4 minutes showed that the oxidizability increased from no vulcanization to 3 minutes' vulcanization, and then decreased with further vulcanization.

The results show, then, that slight vulcanization renders rubber-diazoaminobenzene mixtures very susceptible to oxidation, but that more prolonged heating gives vulcanizates which are much less readily oxidized.

Influence of the percentage of diazoaminobenzene (*DB series*).—Figures 5 and 5a summarize the results of the experiments.

With low percentages of diazoaminobenzene, the oxidizability, which was at first high, decreased, passed through a minimum for 5–7 parts of diazoaminobenzene, and then increased again slightly.

The oxidizability of the unvulcanized mixtures in this same DB series was also measured, but Figure 5 shows only the curves representing the mixtures containining 1, 5 and 20 parts of diazoaminobenzene. The rates of oxidation of the various samples were almost the same up to about 100 mm. ascent of the mercury manometer, *i.e.*, about 25 hours at 80° C was required under the particular conditions. The higher the percentage of diazoaminobenzene, the faster was the rate of vulcanization, and the reaction was characterized by liberation of nitrogen, which vitiated the measurements by counterbalancing the absorption of oxygen, and even causing the mercury column to descend again as happened with the raw DB_7 mixture.

It shoud be interesting to determine what percentage of diazoaminobenzene is combined, for it seems probable that there is in this process something other than the simple polymerizing power suggested by Levi[14]. This would make it possible to decide whether to attribute the plateau effect of oxidizability to a limiting reactivity of the diazoaminobenzene.

CHLORANIL

As already mentioned, Fisher has shown that quinones, particularly halogenated quinones, vulcanize rubber satisfactorily, and that higher halogenated derivatives, such as tetrachloro-*p*-benzoquinone, bring about this same vulcanizing effect even at room temperature within a few months.

As an example of this group of compounds, chloranil was chosen, a crude form of which is obtained in the preparation of tetrachlorobenzoquinone and contains a little of the trichlor derivative.

The addition of chloranil alone to rubber makes it possible to vulcanize the latter. However, metallic oxides or oxidizing agents increase the effectiveness of chloranil, and therefore in a first series of experiments, mixtures prepared from the base mixture: smoked-sheet rubber 100, chloranil 5, by adding 10 parts (based on the rubber) of zinc oxide, magnesium oxide, lead peroxide, lead chromate, manganese dioxide, potassium permanganate, mercuric oxide, vanadic anhydride, and antimonic anhydride, respectively, were vulcanized.

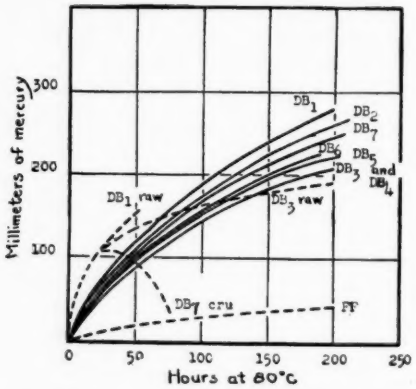


FIG. 5.—Influence of the percentage of diazoaminobenzene on the oxidizability at 80° C. FF is smoked sheet alone.

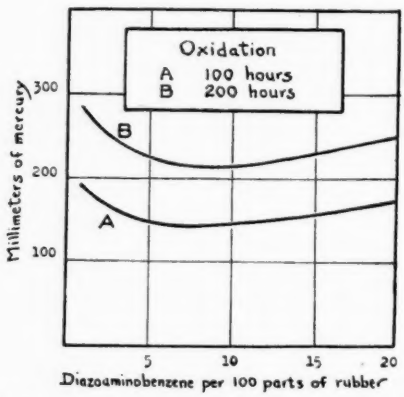


FIG. 5a.—Oxidizability at 80° C as a function of the percentage of diazoaminobenzene in mixtures of the DB series.

Lead chromate, vanadic anhydride and antimonic anhydride retarded vulcanization slightly; the other agents gave vulcanizates of better quality than that of the simple rubber-chloranil mixture. The best results were obtained with manganese dioxide. However, the disastrous effects of this metal on aging are well known, and the vulcanizate became very brittle and at the same time tacky.

From the point of view of oxidizability, manganese dioxide and vanadium anhydride alone stand apart from the other agents in that they give vulcanizates

which have much more tendency to oxidize than those containing the other oxides, the latter of which have no appreciable effect, one way or the other, on the oxidizability of the base mixture of rubber and chloranil.

Finally a series of experiments was carried out with a mixture of smoked-sheet rubber, 100 parts, and magnesium oxide, 30 parts. Table 4 shows the compositions of the various mixtures and their vulcanization.

TABLE 4

Variable time of vulcanization			Variable percentage of chloranil		
Mixture	Chloranil (parts per 100 parts of rubber)	Time of vulcanization at 143° C (min.)	Mixture	Chloranil (parts per 100 parts of rubber)	Time of vulcanization at 143° C (min.)
CA_1	5	5	CB_1	1	30
CA_2	5	10	CB_2	3	30
CA_3	5	30	CB_3	5	30
CA_4	5	60	CB_4	7	30
CA_5	5	120	CB_5	10	30
CA_6	5	240	CB_6	15	30
CA_7	5	360	CB_7	20	30
CA_8	5	480	—	—	—

As with diazoaminobenzene, chloranil gives a very extended plateau of vulcanization; in fact even samples CA_1 and CA_2 were well vulcanized, although a little sluggish. The others also were well vulcanized, and it was necessary to heat the mixtures of the CA series for 6 to 8 hours before a small increase in hardness became evident.

As in the CB series, in which the chloranil was varied and the time of heating maintained the same, sample CB_1 had not set at all, sample CB_2 was still soft, and only with 15 or 20 parts of chloranil did the vulcanizates commence to become harder.

Influence of the time of vulcanization (*CA series*).—From the oxidation measurements the curves represented in Figures 6 and 6a were constructed. The broken curve CA_0 represents the oxidation of the unvulcanized mixture.

At the beginning, this raw mixture was oxidized more rapidly than were the vulcanized samples. The slope of the curve then decreases, but this is probably attributable to fusion of the rubber, which diminishes the surface in contact with oxygen.

The diagrams show clearly that uncombined chloranil has a rather pronounced proöxygenic effect on rubber, but that this effect becomes progressively less as heating is continued and more chloranil enters into reaction. This is then the same phenomenon, but to a lesser extent, that was observed earlier with benzoyl peroxide[19].

Influence of the proportion of chloranil (*CB series*).—Figures 7 and 7a summarize the results of oxidation measurements of a series of mixtures vulcanized for 30 minutes at 143° C, in which the chloranil was varied from 0 to 20 parts. On Figure 7 have also been added the oxidation curves of four of these unvulcanized mixtures, as well as the oxidation curve of sample CB_0, containing no chloranil, but heated for 30 minutes at 143° C.

The following conclusions may be drawn from these results:

(1) The oxidizability of an unvulcanized mixture is always greater than that of the same mixture after vulcanization.

(2) The higher the proportion of vulcanizing agent, the greater the oxidizability of the heated mixture.

However, the curves in Figure 7a have by no means the same general course as those obtained under similar conditions by the use of benzoyl peroxide. They indicate that chloranil is more easily transformed than benzoyl peroxide or else that it combines in greater proportions, so that, with relatively low proportions of vulcanizing agent, there is not enough free chloranil remaining to exert its powerful proöxygenic action.

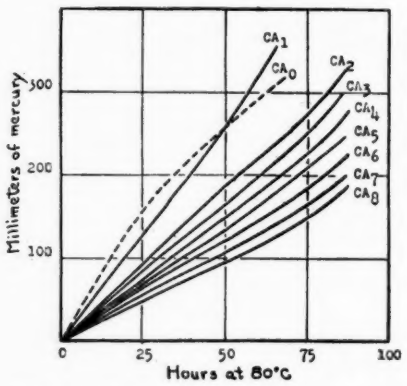


FIG. 6.—Influence of time of vulcanization at 143° C on the oxidizability at 80° C of mixtures containing chloranil. CA_0 is the raw mixture.

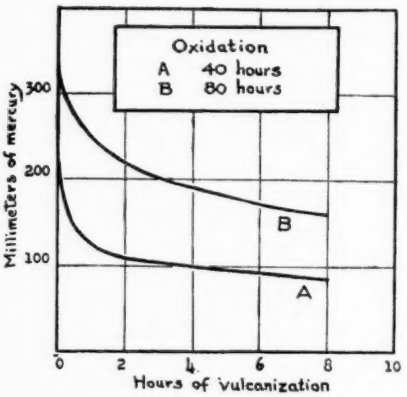


FIG. 6a.—Oxidizability at 80° C as a function of the time of vulcanization at 143° C of chloranil mixtures of the CA series.

QUINONE HALOIMINES

Dichloroiminoquinone was chosen as representative of this type of reagent because it had already been studied by Fisher[15] and by Spence and Ferry[17]. It was of interest to determine whether a compound of this type behaves in the same way as diazoaminobenzene, since Fisher concluded that diazoaminobenzene probably owes its activity to a rearrangement to the imine form:

$$\underset{\text{diazoaminobenzene}}{C_6H_5N:N\cdot NHC_6H_5} \longrightarrow \underset{\text{p-aminoazobenzene}}{C_6H_5N:NC_6H_4NH_2} \longrightarrow \underset{\text{p-quinone-N-anilinodiimine}}{C_6H_5NH\cdot N:C_6H_4:NH\cdot}$$

However, with haloimines, the oxidizability is relatively high, as will be described later[20] and as may be seen in Figure 13, perhaps because of the presence of the halogen. It might therefore have been preferable to make the comparison with the use only of a quinoneimine, and it is intended to complete this study later.

In any event dichloroiminoquinone is, like chloranil and diazoaminobenzene, a very active vulcanizing agent, and it gives a broad plateau of vulcanization.

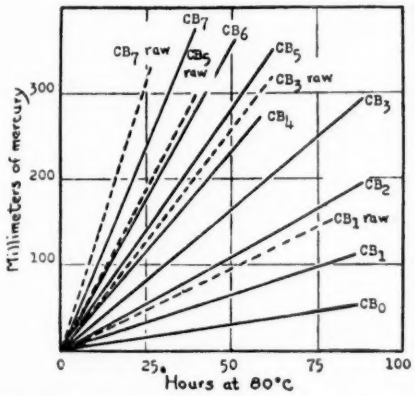


FIG. 7.—Influence of percentage of chloranil on the oxidizability at 80° C.

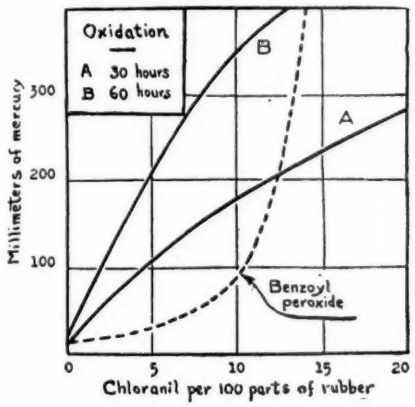


FIG. 7a.—Oxidizability at 80° C as a function of the percentage of chloranil for mixtures of the CB series.

The samples listed in Table 5 were prepared for this series of experiments. Only sample QB_1 was still unvulcanized, and had merely set. Sample QB_2 was still a little sluggish; the other samples were well vulcanized. However, after 1 hour or more of heating, and also with a dichloroiminoquinone content of 15 parts or more, the products tended to be fragile. It should be mentioned that these mixtures were difficult to remove from the molds because of their tendency to adhere to the metal.

Influence of the time of vulcanization (QA series).—Figures 8 and 8a summarize the results of the oxidation measurements. There has been added to

TABLE 5

Variable time of vulcanization			Variable proportion of dichloroiminoquinone		
Mixture	Quinone (parts per 100 parts of rubber)	Time of vulcanization at 143° C (min.)	Mixture	Quinone (parts per 100 parts of rubber)	Time of vulcanization at 143° C (min.)
QA_1	5	5	QB_1	1	30
QA_2	5	10	QB_2	3	30
QA_3	5	20	QB_3	5	30
QA_4	5	30	QB_4	7	30
QA_5	5	60	QB_5	10	30
QA_6	5	120	QB_6	15	30
QA_7	5	240	QB_7	20	30
QA_8	5	360	—	—	—
QA_9	5	480	—	—	—

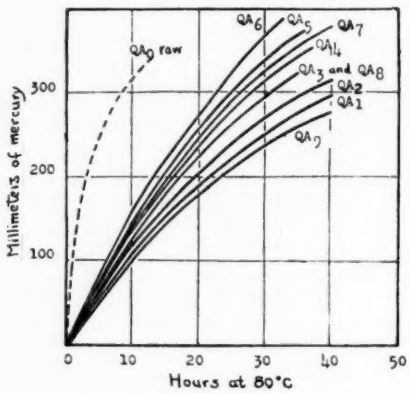


FIG. 8.—Influence of time of vulcanization at 143° C on the oxidizability at 80° C of mixtures containing dichloriminoquinone. QA_0 is the raw mixture.

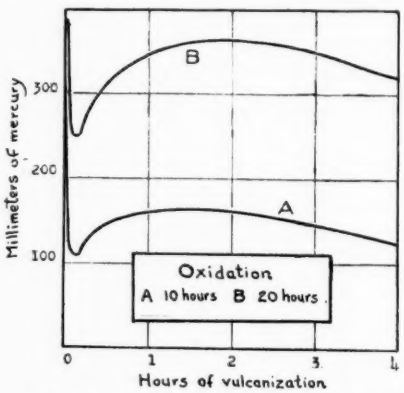


FIG. 8a.—Oxidizability at 80° C as a function of the time of vulcanization at 143° C of the dichloroiminoquinone mixtures of the QA series.

Figure 8 a curve representing the oxidation of mixture QA_0, which was the unvulcanized sample. It will be seen that this unvulcanized mixture was considerably more easily oxidized than the mixtures which had been heated. Dichloroiminoquinone is consequently a proöxygenic agent.

The effect of heating on the oxidizability is rather interesting. The rate of oxidation was considerably diminished by heating for a short time. With further heating the rate of oxidation increased, passed through a maximum rate for an approximate time of heating of 2 hours, and finally decreased again. On the whole it appears that in this case diaminobenzene and chloranil take part in a rather complex set of reactions, as would be expected. This example shows clearly the multiplicity of reactions which take place, and the difficulty of drawing any definite conclusions, even in the case of such a simple mixture as that used in the present work.

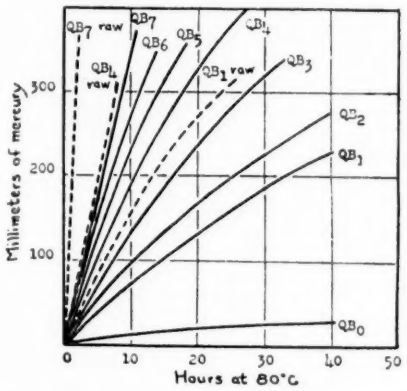


FIG. 9.—Influence of percentage of dichloroiminoquinone on the oxidizability at 80° C.

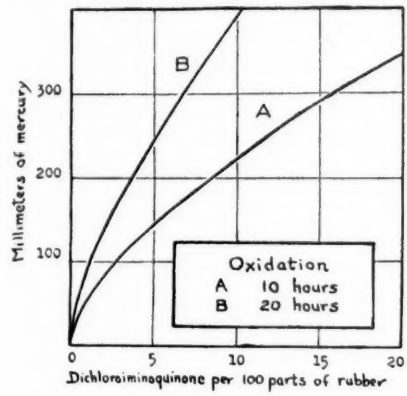


FIG. 9a.—Oxidation at 80° C as a function of the percentage of dichloroiminoquinone in mixtures of the QB series.

Influence of the percentage of dichloriminoquinone (QB series).—Figures 9 and 9a represent the oxidation measurements. Figure 9 includes, in addition, curves representing mixture QB_0, which is simply smoked-sheet rubber masticated and then heated for 30 minutes at 143° C; it includes also curves of the unvulcanized mixtures containing 1, 7 and 20 parts of dichloroiminoquinone.

Instead of finding, as was true of the influence of the time of vulcanization, an effect intermediate between that given by diazoaminobenzene and by chlo-

ranil, the results obtained with dichloriminoquinone and with chloranil were the same. This would appear to confirm the preceding remarks, *viz.*, that like chloranil, a considerable part of the dichloriminoquinone can combine with rubber or be otherwise transformed, whereas diazoaminobenzene shows a plateau of reactivity.

AN AMINE AND AN OXIDIZING AGENT

As representative of a combination of an amine and an oxidizing agent, a rubber mixture described by Fisher was chosen because it is particularly interesting in that it contains both an antioxygenic substance *N,N'*-di-β-naphthyl-*p*-phenylenediamine, and a proöxygenic substance, lead peroxide.

According to Fisher, vulcanization should, in this case, lead theoretically to the formation of quinoneimine, which would then function as the true vulcanizing agent. Actually these two compounds are effective only when they are used together.

On the other hand, it could well be asked, and it has been found to be true that tests in which the time of heating was varied seem to confirm the hypothesis as to whether the peroxide is the vulcanizing agent and the amine a catalyst or accelerator of this vulcanizing action.

TABLE 6

	Mixture	Amine (parts per 100 parts of rubber)	Lead peroxide (parts per 100 parts of rubber)	Time of vulcanization at 143° C (min.)
Variation in the time of vulcanization	NA_1	7.5	30	5
	NA_2	7.5	30	10
	NA_3	7.5	30	15
	NA_4	7.5	30	30
	NA_5	7.5	30	45
	NA_6	7.5	30	60
	NA_7	7.5	30	120
	NA_8	7.5	30	300
	NA_9	7.5	30	480
Variation in the proportion of *N,N'*-d-β-naphthyl-*p*-phenylenediamine	NB_1	1	30	60
	NB_2	2.5	30	60
	NB_3	5	30	60
	NB_4	7.5	30	60
	NB_5	10	30	60
	NB_6	15	30	60
	NB_7	20	30	60
	NB_8	50	30	60
Variation in the proportion of lead peroxide	NC_0	7.5	0	120
	NC_1	7.5	5	120
	NC_2	7.5	10	120
	NC_3	7.5	20	120
	NC_4	7.5	50	120

Three series of experiments were carried out, with variation in the time of vulcanization, proportion of amine, and proportion of lead peroxide. Table 6 gives the compositions of the various mixtures and the heating conditions.

Mixture NA_1 was barely set and was filled with bubbles; NA_2 and NA_3 were soft and slightly porous; the other products of the NA series were well vulcanized. The dark red color which was characteristic of the unvulcanized

mixtures did not remain after an hour's heating, and products heated longer than this were brown.

In the NB series, samples NB_1 to NB′ were well vulcanized, but NB_6, NB_7 and NB_8 were soft and porous to an increasing degree with increase in the percentage of *N,N′*-di-*β*-naphthyl-*p*-phenylenediamine. With respect to color, NB_1, NB_2 and NB_3 were brown; the others of the NB series were red.

Finally in the NC series, samples NC_0 and NC_1 showed no evidence of vulcanization; NC_2 had just set; NC_3 and NC_4 were well vulcanized, but NC_4 was at the same time somewhat fragile. NC_0 and NC_1 were red; NC_2, NC_3 and NC_4 were brown.

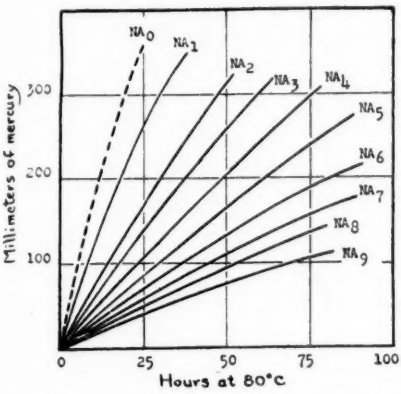


FIG. 10.—Influence of time of vulcanization at 143° C on the oxidizability at 80° C of mixtures containing *N,N′*-di-*β*-naphthyl-*p*-phenylenediamine and lead peroxide. NA_0 is the raw mixture

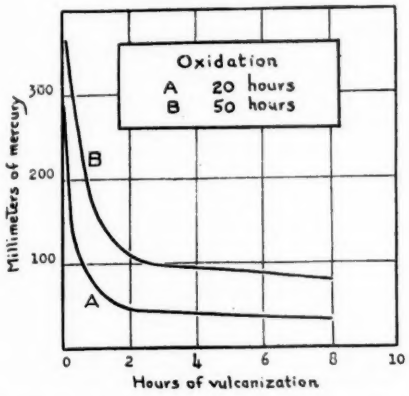


FIG. 10a.—Oxidation at 80° C as a function of the time of vulcanization at 143° C of mixtures containing *N,N′*-di-*β*-naphthyl-*p*-phenylenediamine and lead peroxide of the NA series.

Influence of the time of vulcanization (NA series).—The results of the oxidation measurements are shown in Figures 10 and 10a. Figure 10 includes also the oxidation curve of the unvulcanized mixture NA_0. It shows that the proöxygenic power of lead peroxide far exceeds the antioxygenic action of the amine.

According to the curves in Figures 10 and 10a, the oxidizability decreases greatly with increase in the time of vulcanization and then tends toward a minimum. The curves in Figure 10a resemble closely those which were obtained with the benzoyl peroxide mixtures. This would seem to lend support to the hypothesis suggested at the beginning of this section. As a matter of fact, according to the experiments to be described, it would seem necessary to explain the decrease in oxidizability in the following manner. The first part of the curve, which has a steep slope, indicates decomposition of the lead per-

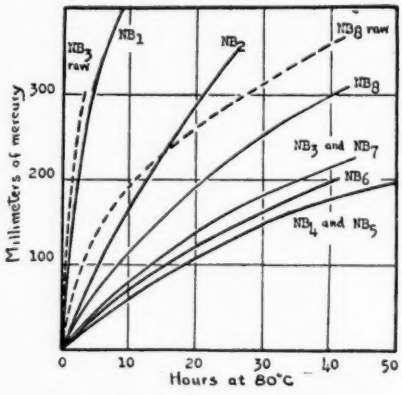


FIG. 11.—Influence of the percentage of *N,N'*-di-β-naphthyl-*p*-phenylenediamine on the oxidizability at 80° C of mixtures containing this amine with lead peroxide.

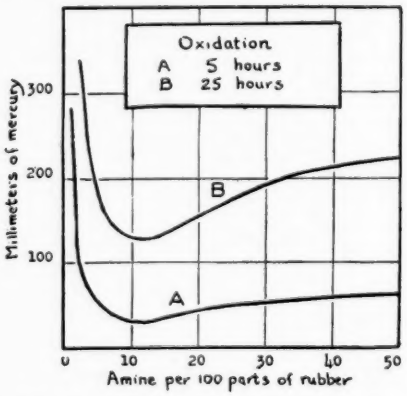


FIG. 11a.—Oxidation at 80° C as a function of percentage of *N,N'*-di-β-naphthyl-*p*-phenylenediamine of mixtures containing this amine and lead peroxide of the NB series.

oxide, with simultaneous formation of quinoneimine and resultant progressive vulcanization. The next part of the curve, which has a relatively slight slope, represents, after entrance into the reaction of all the *N,N'*-di-β-naphthyl-*p*-phenylenediamine, a simple progressive decomposition of the lead peroxide under the influence of heat.

Influence of the proportion of N,N'-di-β-naphthyl-p-phenylenediamine (NB series).—Figures 11 and 11a show the results of the oxidation measurements.

Figure 11 includes also the oxidation curves of two unvulcanized mixtures containing 5 and 50 parts, respectively, of the amine.

It will be seen immediately that the unvulcanized mixtures were oxidized more rapidly than the corresponding vulcanized mixture, even with 50 parts of amine, the antioxygenic effect did not counterbalance the proöxygenic effect of the lead peroxide.

As to the differences in oxidizability of the vulcanized mixtures, an interesting effect was observed. The oxidizability decreased rapidly at first, probably

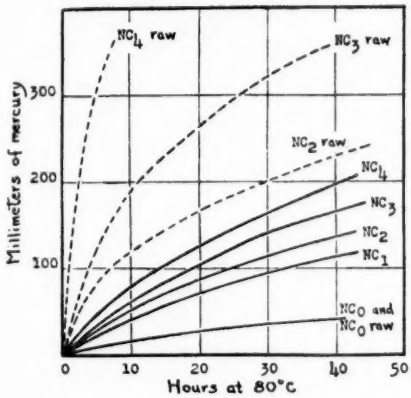


FIG. 12.—Influence of the percentage of lead peroxide on the oxidizability at 80° C of mixtures containing *N,N'*-di-β-naphthyl-*p*-phenylenediamine and lead peroxide.

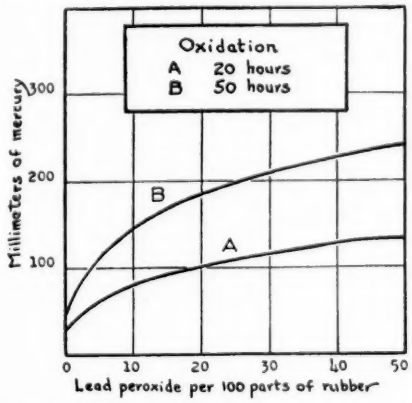


FIG. 12a.—Oxidizability at 80° C as a function of the percentage of lead peroxide in mixtures containing *N,N'*-di-β-naphthyl-*p*-phenylenediamine and lead peroxide of the NC series.

because of a progressive diminution in the amount of free lead peroxide; then it passed through a minimum value, and finally increased noticeably. This final increase corresponded to a state of vulcanization which was not advanced, because, as has been described, with more than 10 parts of *N,N'*-di-β-naphthyl-*p*-phenylenediamine, the mixtures became progressively softer and more porous. It is possible that the amine, which is an antioxygenic substance, is transformed completely into quinoneimine, the excess of which, not entering

into the reaction, functions as a proöxygenic agent, *i.e.*, the part played by the amine in the oxidative effect is simply a reverse one, whereby it magnifies the actual increase in its percentage. In other words the amine may lead to some sort of reversion in the mixture, with resulting liberation of the proöxygenic quinoneimine. It is hazardous, however, on the basis of this single series of experiments, to draw any conclusions as to the correct answer to this problem.

Influence of the proportion of lead peroxide (NC series).—Figures 12 and 12a show the results of oxidation measurements carried out with these mixtures. The broken curves in Figure 12 represent the unvulcanized mixtures containing 10, 20 and 50 parts, respectively, of lead peroxide. In the case of the mixture containing no lead peroxide, the oxidation curve of the unvulcanized mixture and that of the heated mixture (which had not become vulcanized) are practically coincident. The results of these tests lead to two conclusions:

(1) Mixtures which contain lead peroxide are always more oxidizable before they have been heated than after they have been heated.

(2) The higher the proportion of lead peroxide, the greater the oxidizability of mixtures after vulcanization.

These two conclusions are in harmony with the previous observations. It should be noted, however, that the curves in Figure 12a are not at all similar to those obtained when the percentage of benzoyl peroxide was varied. The latter curves show a very well defined autocatalytic course. In the present case, on the contrary, it appears that the proöxygenic action of the lead peroxide tends toward a plateau when the percentage of this peroxide in the mixture is increased.

In any event, it is obvious from the three series of experiments that it is possible, by adjusting properly the proportions of *N,N'*-di-β-naphthyl-*p*-phenylenediamine and lead peroxide, as well as the vulcanizing conditions, to obtain by such a method vulcanizates which have relatively little tendency to oxidize.

COMPARISON WITH SULFUR MIXTURES

The different vulcanizing agents which have been studied in the present work give vulcanizates whose mechanical properties appear to be almost the same as those of simple rubber-sulfur mixtures. It was interesting to make a direct comparison of the tendencies of these two types of vulcanizates to oxidize. In this comparison the samples which were vulcanized to the most nearly correct point were in each case chosen for the oxidation measurements.

It would have been illogical, however, to make a direct comparison of a rubber-sulfur vulcanizate with another vulcanizate to which an antioxygenic agent had been added, whether directly as in the case of *N,N'*-di-β-naphthyl-*p*-phenylenediamine or by the probable formation during heating of an antioxygenic agent, *e.g.*, diphenylamine during vulcanization by diazoaminobenzene or tetrachlorhydroquinone during vulcanization by chloranil.

Rubber-sulfur mixtures containing these agents or allied compounds were also prepared, and their tendencies to oxidize were compared with those of the other vulcanizates.

Table 7 gives the compositions of the various mixtures and times of heating at 143° C.

To avoid any danger of misinterpretation, it is well to point out that the majority of the experiments which have been described in the present work were

TABLE 7

Mixture	Vulcanizing agent: Compound	Vulcanizing agent: Parts per 100 parts of rubber	Other agent: Compound	Other agent: Parts per 100 parts of rubber	Time of vulcanization at 143° C (min.)
S	Sulfur	6	—	—	360
SH	Sultur	6	Hydroquinone	5	360
SD	Sulfur	6	Diphenylamine	5	360
SN	Sulfur	6	*N,N'*-di-β-naphthyl-*p*-phenyldiamine	5	360
VA_4	Selenium	125	Zinc oxide *p*-Nitrosodimethylaniline	5 3	480
DA_4	Diazoaminobenzene	5	—	—	30
CA_4	Chloranil	5	Magnesium oxide	30	60
QA_3	Dichloroiminoquinone	5	—	—	20
NA_7	*N,N'*-di-β-naphthyl-*p*-phenylenediamine Lead peroxide	7.5 30	—	—	120

carried out in glass manometers. In the construction of each of these, care was taken that the tubes were of equal and uniform size. However, there was variation between one apparatus and another to such an extent that it is not possible to transpose an oxidation curve from one diagram to another, and reliable comparisons are possible only within one individual series of experiments. It should not be surprising then, if in Figure 13, which shows the

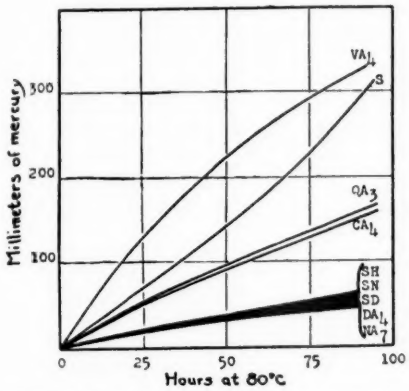


FIG. 13.—Comparison of oxidizabilities at 80° C of vulcanized mixtures.

S sulfur
VA_4 selenium
DA_4 diazoaminobenzene
CA_4 chloranil
QA_3 dichloroiminoquinone
NA_7 *N,N'*-di-β-naphthyl-*p*-phenylenediamine and lead peroxide
SH, SN, SD sulfur and an antioxygenic agent

results of oxidation measurements of the mixtures given in Table 7, some of the curves are not exact replicas of those in the preceding diagrams.

As may be seen in Figure 13, a comparison of the rates of oxidation of the different vulcanizates proved to be particularly interesting. It is evident, for example, that: (1) the rubber-sulfur and the rubber-selenium mixtures oxidized at practically the same rates;

(2) mixtures vulcanized by diazoaminobenzene or by an amine and an oxidizing agent behaved like rubber-sulfur mixtures protected by various antioxygenic substances;

(3) mixtures vulcanized by dichloroiminoquinone or by chloranil showed rates of oxidation intermediate between those of the preceding two groups.

CONCLUSIONS

If it is attempted to sum up the important results obtained in the present study, the following points seem to be well established.

First of all, with respect to selenium. Whether the oxidizabilities of products vulcanized by selenium alone or of products vulcanized by a mixture of selenium and sulfur are measured, they show the same general behavior as do mixtures vulcanized by sulfur alone. It is the percentage of vulcanizing agent in combined form that governs the oxidizability, for the addition of selenium to sulfur increases this oxidizability. If part of the sulfur is replaced by selenium, there is a decrease in the oxidizability, but this can be explained by the lesser reactivity of the selenium, as a result of which the product is vulcanized to a less extent. It is not true, then, that, for a given state of cure, selenium improves aging.

The case of diazoaminobenzene is a more complicated one. This compound decomposes during vulcanization, with liberation of nitrogen and probable formation of antioxygenic substances such as diphenylamine. Diazoaminobenzene itself is a proöxygenic substance, and mixtures containing it which have been heated only a short time have a strong tendency to oxidize. With longer heating, complete decomposition of the diazoaminobenzene inevitably takes place, and the oxidizability becomes established at a relatively small value.

In the same way, with chloranil and with dichloroiminoquinone, the reaction leads to the formation of antioxygenic substances, and when vulcanization is carried to a sufficient point, the oxidizability decreases.

It should be mentioned that such a prolongation of the time of heating does not have any harmful effect on the mechanical properties of the vulcanizate. Actually all the agents gave a remarkably broad plateau, and no appreciable differences in mechanical properties were found over a wide range of heating times, *e.g.*, 30 minutes to 8 hours.

As for the joint use of an amine and an oxidizing agent, such as *N,N'*-di-β-naphthyl-*p*-phenylenediamine and lead peroxide, it will be found that, here too, with increase in the time of vulcanization the tendency to oxidize decreases to a minimum, probably as a result of progressive decomposition of the peroxide. If it is attempted to counteract this proöxygenic action directly by the addition of a large amount of the amine, it will be found that, on the contrary, vulcanization becomes less and less effective and the oxidizability increases. However, by adjusting the proportions of amine and of oxidizing agent judiciously, it is possible to obtain products the resistance of which to oxidation is remarkably good.

In a special experiment, a direct comparison was made of samples vulcanized with the agents described in the present work and a simple rubber-sulfur vulcanizate, both unprotected and protected by different antioxygenic substances, including diphenylamine, hydroquinone and *N,N'*-di-β-naphthyl-*p*-phenylenediamine. By plotting the results, the curves shown in Figure 13 were obtained. These curves make particularly clear the fact that it is possible, by means of certain vulcanizing agents, *e.g.*, diazoaminobenzene or an amine plus an oxidizing agent, to obtain vulcanizates which have as much resistance to oxidation as that of rubber-sulfur vulcanizates containing an

antioxygenic substance. This is not true of nitro compounds, with which even ordinary antioxygenic agents have only a relatively slight protective action.

A thorough investigation of these vulcanizing agents is then of importance, not only in helping to explain the mechanism of vulcanization itself but also because of the possibilities of its leading to various practical applications.

REFERENCES

[1] Dufraisse and Étienne, *Rev. gén. caoutchouc* **14**, 9 (1937); **15**, 12 (1938); RUBBER CHEM. TECH. **11**, 282 (1938).
[2] Ingmanson and Kemp, *Ind. Eng. Chem.* **30**, 1168 (1938); Kemp, Ingmanson and Mueller, *Ind. Eng. Chem.* **31**, 1472 (1939).
[3] Stevens and Gaunt, *Proc. Rubber Tech. Conf. London*, **1938**, p. 686.
[4] Blake and Bruce, *Proc. Rubber Tech. Conf. London*, **1938**, p. 736.
[5] Dufraisse and Le Bras, RUBBER CHEM. TECH. **12**, 805 (1939).
[6] Dufraisse, RUBBER CHEM. TECH. **11**, 268 (1938).
[7] Dufraisse and LE BRAS, *Caoutchouc et plastiques* **2**, 37 (1939).
[8] Dufraisse and Compagnon, *Rev. gén. caoutchouc* **18**, 39 (1941); RUBBER CHEM. TECH. **19**, 329 (1946).
[9] Boggs, *Ind. Eng. Chem.* **10**, 117 (1918).
[10] Boggs and Follansbee, *Trans. Inst. Rubber Ind.* **2**, 272 (1926–1927).
[11] R. T. Vanderbilt Co., *Vanderbilt News* **6**, No. 2, 6 (1936).
[12] Buizov, *J. Russian Phys.-Chem. Soc.* **53**, 166 (1921).
[13] Fisher, Belvedere Chemical Co., Ltd., French patent 806,500 (1936).
[14] Levi, *Gomma* **1**, 4 (1937); RUBBER CHEM. TECH. **10**, 471 (1937).
[15] Fisher, *Ind. Eng. Chem.* **31**, 1381 (1939).
[16] Fisher and Naugatuck Chemical Co., French patent 740,978 (1932).
[17] Spence and Ferry, *J. Am. Chem. Soc.* **59**, 1648 (1937).
[18] Blake, *Ind. Eng. Chem.* **22**, 744 (1930).
[19] Dufraisse and Le Bras, RUBBER CHEM. TECH. **12**, 821 (Figure 9a) (1939).
[20] See later section on a comparison with sulfur mixtures, and Figure 13.

VULCANIZATION REACTIONS IN BUTYL RUBBER *

Action of Dinitroso, Dioxime, and Related Compounds

JOHN REHNER, JR., AND PAUL J. FLORY

ESSO LABORATORIES, STANDARD OIL DEVELOPMENT COMPANY, ELIZABETH, N. J.

In the three decades following Ostromislensky's discovery that natural rubber could be vulcanized by polynitro derivatives of benzene[1], vulcanization by substances other than sulfur has been the subject of many investigations. Aside from polynitro compounds, the materials whose vulcanizing activities have been most completely studied from the standpoint of the chemical reactions involved, include benzoyl peroxide, tetramethylthiuram disulfide, quinones, and various halogenated and nitrogen derivatives of quinones; *e.g.*, quinone imines, quinone dioxime, and alkyl ethers of quinone oximes. Ostromislensky[2] and Fisher[3] have published discussions and bibliographies of the behavior of these substances in natural rubber.

Although the chemical reactions involved depend on the vulcanizing agent employed, Fisher[3] proposed a general theory, suggested by Ostromislensky for the more limited case of vulcanization by peroxides and by polynitro compounds, that the fundamental action common to all vulcanization is oxidation-reduction. He considers that, where two states of oxidation of the vulcanizing agent are possible—for example, in quinone and hydroquinone—the reduced agent (presumed to be formed by the action of nonrubber components) reacts with the rubber hydrocarbon at the double bonds; this addition product is then oxidized to give the vulcanizate. In support of his view, he points out that reduction products have been found and identified in vulcanizates prepared with tetramethylthiuram disulfide (tetramethylthiuram monosulfide), *m*-dinitrobenzene (possibly dinitroazoxybenzene), benzoyl peroxide (benzoic acid), hexachlorodiazoaminobenzene (hexachlorodiphenylamine), quinone (hydroquinone), and tetrachloroquinone (tetrachlorohydroquinone).

Nonsulfur vulcanization of synthetic rubbers are proved to be of considerable importance. The use of basic oxides for vulcanizing polychloroprene and ethylene dichloride-sodium polysulfide condensation polymers, and of such substances as tetramethylthiuram disulfide in butadiene polymers and copolymers are familiar examples. More recently it has been found in these laboratories[4] that Butyl rubber is rapidly vulcanized in the presence of oxidizing agents by quinone dioxime and its esters. The behavior of this and related substances has been extensively explored.

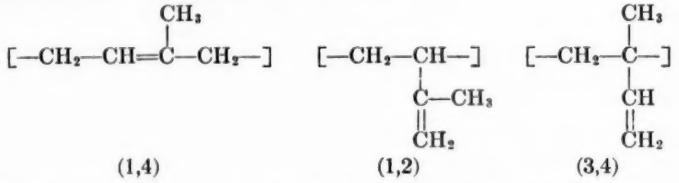
In contrast to the abundance of technical information available on various types of nonsulfur vulcanization, relatively little has been disclosed concerning the chemical reactions involved. The present investigation was undertaken in an attempt to determine the nature of the reactants actually responsible for the vulcanization of Butyl by dioxime-type vulcanizing agents, and the manner

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 38, No. 5, pages 500–506, May 1946. The present address of P. J. Flory is The Goodyear Tire and Rubber Co., Akron, Ohio.

in which they react to produce vulcanization. The results obtained also bear on related vulcanization processes in other rubbers.

REACTIONS WITH OLEFINS

In general, if diolefins such as isoprene are polymerized or copolymerized, the diolefin may be expected to enter the polymer chain either by 1,4 or 1,2 or 3,4 addition to yield the following chain units:



(1,4) (1,2) (3,4)

An important difference, as far as vulcanization is concerned, lies in the position of the essential double bond in the various structures; that in the 1,4 units is internally situated, whereas the 1,2 and 3,4 units possess terminal $=CH_2$ groups. A difference in reactivity with respect to vulcanizing agents would be expected between these types of double bond.

Therefore, an experiment was run to react quinone dioxime with each of two small molecular analogs, 2-methyl-2-butene and 1-pentene, the structures of which correspond to the respective isoprene units shown above. Mixtures of these olefins (20 cc.) with the dioxime (6.6 grams) and, in some cases, with added red lead oxide (Pb_3O_4), were sealed in glass tubes and heated at 120–125° C for 4 and 24 hours. The reaction mixtures were then filtered, the residues washed with a known amount of isopentane, and the combined filtrates evaporated to dryness. The yields of residue (Table I) have been corrected for the solubility of quinone dioxime in the hydrocarbons employed.

TABLE I

REACTIONS OF QUINONE DIOXIME WITH 1-PENTENE AND WITH 2-METHYL-2-BUTENE

Olefin	Pb_3O_4 (grams)	Hours at 120–125° C	Residue in Filtrate[a] (mg.)
1-Pentene	..	4	0
	..	24	−1
	33	4	−3
	33	24	1
2-Methyl-2-butene	..	4	11
	..	24	24
	33	4	37
	33	24	61

[a] Corrected for dioxime solubility.

The small amounts of residue obtained on evaporation of the filtrates were tarry. In some of the trials it was possible to detect a sharp quinonelike odor. The results in the last column of Table I indicate that, within the probable experimental error, no reaction occurred in the experiments with 1-pentene; this explains the independence of these corrected yields on the length of heating or presence of red lead oxide. In contrast, the yields in the experiments with 2-methyl-2-butene increased with time of heating; furthermore, the presence of red lead oxide increased the amount of product several fold. The low absolute

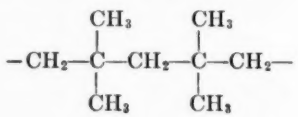
yields obtained are doubtless due to the minute solubility of the dioxime which, with the lead oxide, settled in the bottom of the tube. The solubility in the olefins were determined to be of the same order (6 and 18 mg. per 100 cc. in 2-methyl-2-butene and 1-pentene, respectively, at room temperature).

Under the conditions of these experiments it appears that the 2-methyl-2-butene double bond, which corresponds to that in the 1,4 isoprene unit, is reactive toward quinone dioxime, and the reaction is enhanced by the presence of red lead oxide; on the other hand, the 1-pentene double bond, which corresponds to that in the 3,4 isoprene unit, is not reactive, even in the presence of the lead oxide.

REACTION OF QUINONE DIOXIME WITH BUTYL

Unless otherwise stated, experiments reported in this paper were carried out with a Butyl rubber prepared by low-temperature copolymerization of isobutylene with a small proportion of isoprene. This product had a viscosity-average molecular weight of 450,000, and a diolefin content of about 0.6 mole-per cent of the structural units.

Previous investigations in these laboratories[6] and elsewhere[7] have established that polyisobutylene consists of long chains in which the isobutylene units are joined in the head-to-tail configuration:



Butyl rubber possesses the same chain structure, with occasional diolefin units interspersed between those of isobutylene. Analysis of this structure by methods based on degradative ozonolysis[8] shows that nearly all the diolefin units occur in the 1,4 position; the proportion of 1,2 or 3,4 units if present, does not exceed 1 per cent. On the basis of the preceding results, the vulcanization reaction is expected to occur at the diolefin units in the rubber molecule.

The following experiments served to show that quinone dioxime alone is not capable of vulcanizing Butyl rubber; an oxidizing agent is required. Milled mixtures of Butyl rubber and the dioxime, with and without added manganese dioxide, were cured as described in Table II, and observations were made of their solubility behavior on mechanical agitation with a large excess of Varsol 1 (mineral spirits with a boiling range of 150–200° C). A fresh sample of cured compound 350–4 was refluxed for 4 days with Varsol 1. Some disintegration occurred, but a large part of the sample remained as a highly swollen but undissolved material. It was possible, on the other hand, to dissolve a sample

TABLE II

EFFECT OF MANGANESE DIOXIDE ON SOLUBILITY OF A BUTYL-DIOXIME MIXTURE

Sample	60-Minute Cure (° C)	Period of Shaking	
		2 days	4 days
350–1[a]	153	Completely dissolved	Completely dissolved
350–4[b]	135	Swollen, not dissolved	Swollen. not dissolved

[a] Butyl rubber 100.0, quinone dioxime 4.0.
[b] Butyl rubber 100.0, quinone dioxime 2.0, MnO_2 1.25.

of 350–1 by allowing it to stand in contact with an excess of the solvent for one day or less at room temperature with occasional gentle shaking. It is apparent from these results, together with others described below, that it is difficult to attribute the behavior of peroxides merely to catalytic effects.

If quinone dioxime were capable of direct vulcanization of Butyl rubber, treatment of a Butyl solution with the dioxime should result in gelation. Portions (25 cc.) of a solution containing 7.5% Butyl in naphtha (boiling range 74–113° C) were sealed in glass tubes with 1.0 gram of quinone dioxime and 3.0 grams of lead dioxide, and were heated 40 hours at 125–130° C. Appropriate controls from which the dioxime or the dioxide had been omitted were given similar treatment. To demonstrate the necessity for chemical unsaturation in the polymer chain, a parallel series of tubes was prepared with naphtha solutions containing 5.0 per cent of polyisobutylene instead of Butyl. The polyisobutylene had a viscosity-average molecular weight of 2,300,000 and a negligible amount of chemical unsaturation, as determined by a modified Wijs method. Observations were also made of the contents of tubes containing similar mixtures at room temperature. Table III gives results of the tests.

TABLE III

EFFECTS OF LEAD DIOXIDE AND OF CHEMICAL UNSATURATION ON GELATION OF SOLUTIONS CONTAINING BUTYL AND QUINONE DIOXIME

Polymer	Substances added	Hours at 125–130° C	Nature of contents
Butyl	None	..	Fluid
	None	40	Fluid
	Dioxime	40	Fluid
	Dioxime + PbO_2[a]	40	Gel
	PbO_2	40	Fluid
Polyisobutylene	None	..	Fluid
	None	43	Fluid
	Dioxime	43	Fluid
	Dioxime + PbO_2	43	Fluid
	PbO_2	43	Fluid

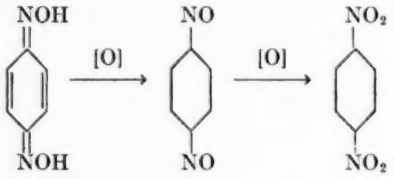
[a] Gelation occurred in this sample on standing overnight at room temperature.

It is evident that neither the dioxime nor the oxidizing agent is capable of causing gelation in Butyl solutions, but the combination is quite active in this respect, even at room temperature. The gel thus obtained was stable to the heat treatment, and although subsequent syneresis took place, intermittent shaking over a period of several weeks did not destroy the structure. From the fact that no gelation occurred in the corresponding polyisobutylene solutions, it is inferred that the isoprene units in the Butyl chains interact during the vulcanization process.

As further evidence for the view that the peroxides enter chemically into the vulcanization reactions, methylethyl ketone extraction of Butyl, vulcanized with quinone dioxime and a peroxide, gave an extract containing a small amount of yellow needles; these needles had a quinonelike odor suggestive of that of some of the residues obtained in the trials with simple olefins. In no case was a sufficient amount of these needles available to allow further purification and analysis. That this substance was not quinone, however, was indicated by the fact that the solubility of quinone in the ketone greatly exceeded that of the extracted substance.

EFFECT OF DINITROSOBENZENE AND RELATED COMPOUNDS

The foregoing experiments led to a consideration of the possibility that the effective vulcanizing agent is an oxidation product of the dioxime. Quinone dioxime can be easily oxidized to form *p*-dinitrosobenzene[9] and this, in turn, can be converted to *p*-dinitrobenzene under more vigorous oxidation:



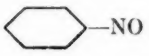
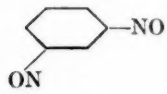
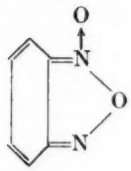
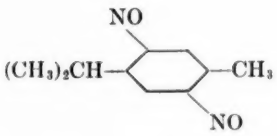
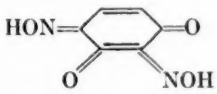
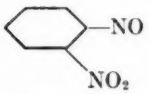
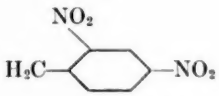
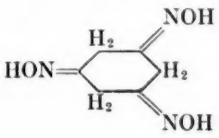
Therefore attempts were made to vulcanize Butyl with these oxidation products and with related substances. Furthermore, dinitrosobenzene possesses an odor and appearance resembling quinone, which suggested that it may have been the substance extracted from the Butyl vulcanizate and mentioned above.

p-Dinitrosobenzene was synthesized by the method of Nietzki and Kehrmann[9]. This substance is an extremely active vulcanizing agent for Butyl rubber. Even when present in amounts of 1 per cent or less, "scorching" on the mill was difficult to avoid except by a relatively cool mixing technique. Oxidizing agents such as metallic or organic peroxides were unnecessary. On the other hand, the *p*-dinitro compound was ineffective, with or without added peroxides. The action of some related compounds as vulcanizing agents for Butyl is indicated in Table IV. They were tested in the recipe: Butyl rubber 100, zinc oxide 5, stearic acid 3, channel carbon black 60, vulcanizing agent 2. Cures ranged from 15 to 120 minutes at 287° F. The inactivity of nitrosobenzene and of *o*-nitronitrosobenzene is ascribable to their monofunctionality, as a result of which cross-linking of adjacent chains is impossible; the inactivity of *o*-dinitrosobenzene is readily understood in view of the likelihood that the latter is not a dinitroso compound but rather a furoxan[10]. A similar misnomer occurs in the case of 2,4-dinitrosoresorcinol, which is considered to be a dioxime[11], as Table IV shows.

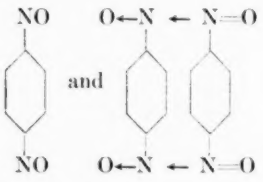
Although the formulas of the nitroso and dinitroso compounds in Table IV are written in the simplest conventional manner, some doubt exists as to their molecular structure. Forster and Fierz[12] suggested, largely on the basis of work with orthodisubstituted derivatives, that the structure ON—⬡—NO is incorrect, and that compounds of this kind should be classified as quinone dioxime peroxides ON=⬡=NO. On stereochemical grounds it is difficult to accept the latter structure. As compounds containing the $\diagup$C—N=O group are characterized by a blue or green color, either in the solid or dissolved state, and by a tendency to associate to colorless bimolecular complexes through the nitrogen atoms of the nitroso groups, Sidgwick[13] concluded that "the compound described as *p*-dinitrosobenzene, although it has the right composition, is almost certainly no nitroso compound". The substance consists of yellow crystals and has a very low solubility in most common solvents. On the other hand, it can be dissolved in hot xylene to give

TABLE IV

VULCANIZING ACTIVITY OF DINITROSO AND RELATED COMPOUNDS IN BUTYL

Compound	Probable monomolecular formula	Vulcanizing activity
Nitrosobenzene		Inactive
p-Dinitrosobenzene		Very active
m-Dinitrosobenzene		Very active
o-Dinitrosobenzene		Inactive
Dinitrosocymene		Very active
2,4-Dinitrosoresorcinol		Inactive
o-Nitronitrosobenzene		Inactive
o-, *m*-, or *p*-Dinitrobenzene		Inactive
2,4-Dinitrotoluene		Inactive
Phloroglucinol trioxime		Inactive

a green solution[14]. In view of these facts, and by analogy with the structure proposed by Hammick[15] for the associated form of nitrosobenzene, the authors consider it likely that, in hydrocarbon solution, *p*-dinitrosobenzene consists of an equilibrium mixture of

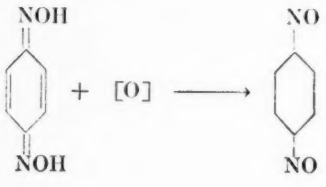


with the equillbrium favoring the bimolecular form. Similar observations and reasoning lead to a rejection of the peroxide structure proposed by Kehrmann and Messinger[16] for *p*-dinitrosocymene in favor of one analogous to that given for *p*-dinitrosobenzene.

Experiments similar to those summarized in Table III were carried out with Butyl solutions containing *p*-dinitrosobenzene, with and without added lead dioxide. It was found that, after standing overnight at room temperature, the viscosity of the Butyl solution increased noticeably, and a firm gel was observed at the interface between the solution and the excess of the slightly soluble *p*-dinitrosobenzene in the bottom of the tube. The same behavior was observed in the tube containing lead dioxide. The gel structure was destroyed on heating for 40 hours at 125–130° C, and was not restored after several days at room temperature. In a parallel experiment with the more soluble *p*-dinitrosocymene, the entire contents of the tube set to a firm gel on standing at room temperature for a day. The gel persisted after heating at 125–130° C for 10 hours, but was solubilized after an additional 17 hours of heating. After the resulting solution had been allowed to rest at room temperature for 24 hours, it was observed that a considerable amount of gel had reformed. Similar experiments with polyisobutylene did not result in gelation in any case.

THEORY OF VULCANIZATION BY POLYNITROSO COMPOUNDS

The preceding experiments show that the chemical reactions involved in the vulcanization of Butyl rubber by quinone dioxime in the presence of oxidizing agents are intimately related to the oxidizability of the dioxime, the properties of the resulting aromatic nitroso groups, and the reactions of the latter with the isoprene units in the polymer chains. The ease with which quinone dioxime can be oxidized to *p*-dinitrosobenzene, the pronounced vulcanizing activity of the latter, and the lack of activity in either the starting substance or in the ultimate oxidation product, *p*-dinitrobenzene, suggest that oxidation of the dioxime to the nitroso state:

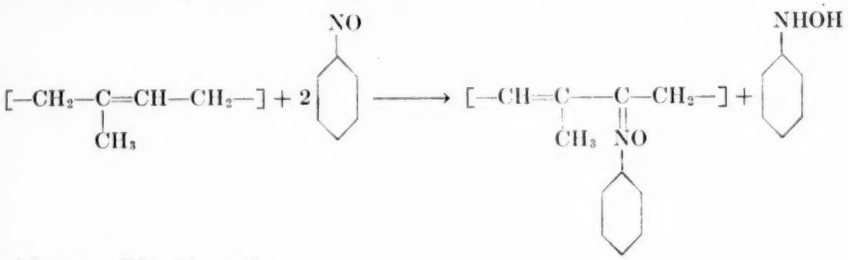


(1)

is the first step in the reactions involved. A detailed examination of the experimental results previously described finds them concordant with this view. The ability, furthermore, of channel carbon black to render the dioxime active may be attributed to the sorbed oxygen in that material. As would be expected, a carbon black relatively free of oxygen, such as Gastex, is ineffective. The facts that Butyl solutions containing the dioxime are gelled only when a peroxide is present, but that gelation occurs with the dinitroso compound even in the absence of added peroxide, are likewise in harmony with the theory. The capacity of dinitrosobenzene to effect vulcanization in relatively small concentrations implies that, when the dioxime is employed, the conversion indicated by reaction 1 need not be, and probably is not, complete.

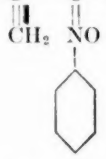
In regard to the cross-linking reactions, very little research has been published on the reactions of nitroso groups with olefinic double bonds, principally by Alessandri, Angeli, Bruni, and coworkers. They studied reactions of nitrosobenzene with safrole, methyleugenol, and other molecules containing the propenyl group[17]. Burkhardt, Lapworth, and Walkden[18] gave the mechanism of these reactions for styrene. With respect to Butyl vulcanization, the resulting phenyl-*N*-phenyl nitrone is unsaturated.

The investigations[19] of the reactions of natural rubber with nitroso compounds are illuminating. Bruni and Geiger showed that nitrosobenzene reacts with the rubber hydrocarbon to give a nitrone of isorubber:

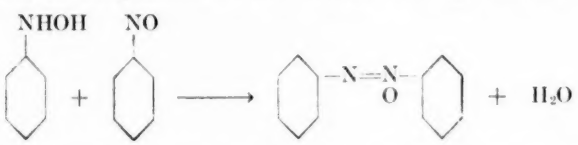


with a possible alternative

structure [—CH_2—C(=CH_2)—C(=NO)—CH_2—] for the nitrone.

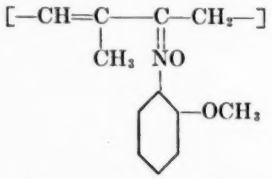


A large amount of azoxybenzene is liberated, according to the reaction:

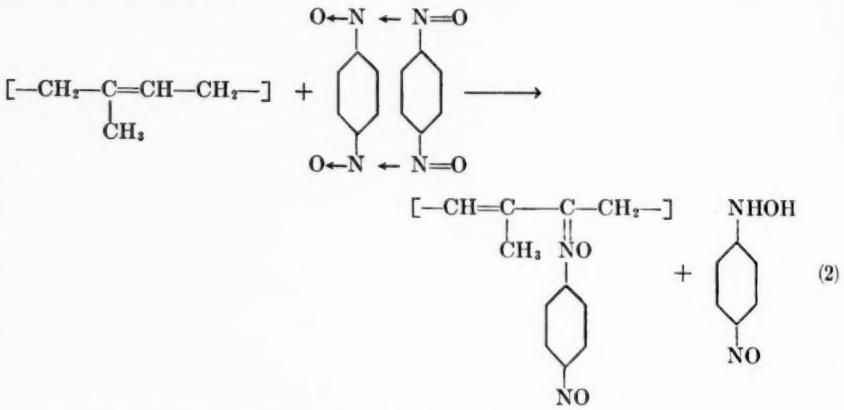


The nitrone contains an olefinic double bond, gives a dibromo derivative, and reacts with phenylhydrazine to give a hydrazone. Bruni and Geiger showed further that nitrosophenols do not react with rubber in the above manner since they are not true nitroso compounds but behave as quinone oximes, O=C_6H_4=NOH. Conversely, the methyl ether of *o*-nitrosophenol, in which the tauto-

meric oxime is not possible, reacts like nitrosobenzene to give the corresponding derivative:

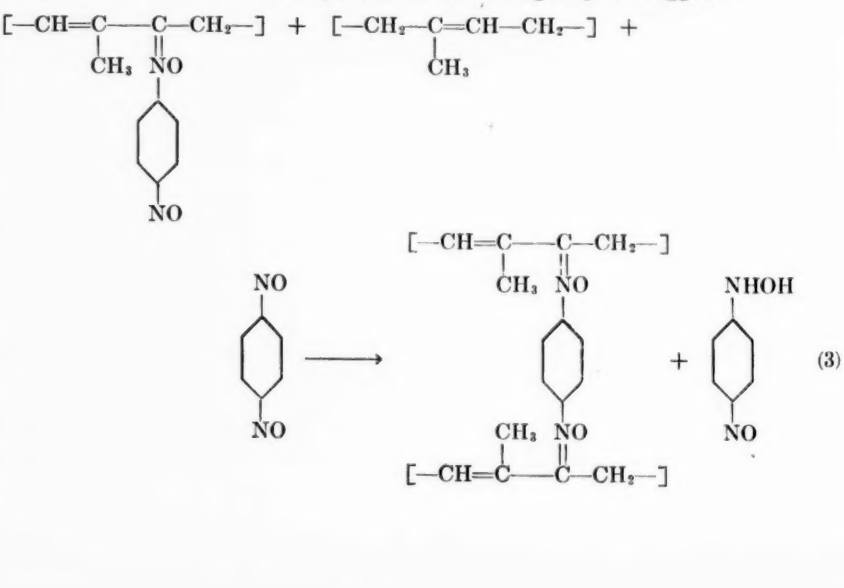


By analogy with the Bruni-Geiger reactions, the authors propose that the second step in the vulcanization process consists of a reaction of the *p*-dinitrosobenzene, formed in reaction 1, with a diolefin unit in a Butyl rubber chain, illustrated as follows:



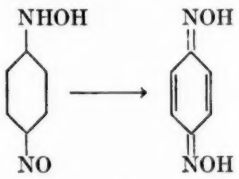
(2)

The bifunctionality of the dinitroso compound then enables crosslinking to occur by a subsequent reaction analogous to Equation 2. The free nitroso group may condense with the diolefin unit of a neighboring chain, a nitroso group of a second dinitrosobenzene molecule being reduced in the process. Thus, for the third and all-important cross-linking step we suggest:



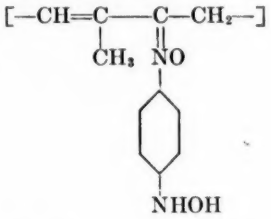
(3)

The *p*-nitrosophenyl hydroxylamine formed in Reactions 2 and 3 has never been isolated. At the instant of formation, it doubtless rearranges rapidly through the migration of a hydrogen atom to give quinone dioxime:

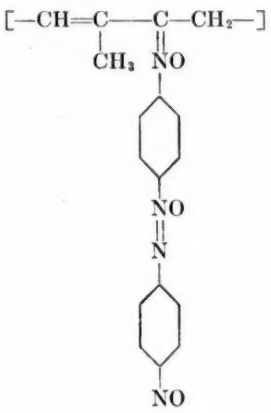


(4)

The above steps are presented merely as a plausible scheme in the light of known reactions of nitroso compounds with unsaturated molecules. The chemistry of the reactions of nitroso compounds is complex and not fully understood at present. Other subsidiary processes doubtless occur. One variation of the above scheme would result from participation in either step 2 or 3 of the second nitroso group of the adduct produced in Equation 2, whereby this group would be reduced to the hydroxylamine:



Rearrangement as in formula 4 is not possible here. However, nitroso compounds react rapidly with hydroxylamines to produce azoxy compounds; the compound in this case is:



(5)

This product possesses a nitroso group potentially capable of condensation with an isoprene unit, according to step 3; or this nitroso group might be reduced, whereupon another azoxy group would be formed. In any event, reaction with another diolefin unit may ultimately occur, although the structure of the cross-linkage is variable, having zero, one, two, or more azoxy units between chains.

CONFIRMATORY EXPERIMENTS

If the vulcanization reactions proceeded in accordance with the above theory, one would expect a Butyl rubber that had been vulcanized with *p*-dinitrosobenzene to be characterized by chemical unsaturation, combined nitrogen, and extractable quinone dioxime. To test these predictions, a 400-gram sample of Butyl containing 3 per cent of *p*-dinitrosobenzene was vulcanized for 2 hours at 125–140° C. The product was then extracted in a Soxhlet apparatus with three solvents, used in rotation, until a limit of extractability was reached, as judged by the color of the extract. The extractions were carried out in an atmosphere of carbon dioxide to minimize oxidative influences. The solvents and the corresponding total extraction periods for each follow: absolute alcohol 232 hours, methanol 168, methylethyl ketone, 407. The extracts were combined and evaporated to a small volume in an atmosphere of nitrogen. The extracted vulcanizate was dried in a vacuum at 70° C until the odor of solvents had entirely disappeared.

Chemical Unsaturation.—A modified Wijs determination showed that the extracted vulcanizate had 2.7 mole-per cent unsaturation, as compared with about 0.6 mole-percent for the Butyl starting material. Experimental difficulties in the determination, the drastic procedure of heating the vulcanizate in Nujol at 179° C to effect solution, and the unknown effect of the C=N or N=O double bond on the Wijs reagent, combined to allow only the qualitative indication that the resulting vulcanizate was unsaturated.

Combined Nitrogen.—The extracted vulcanizate was analyzed by a modified Kjeldahl method and found to contain 0.25 per cent nitrogen. The calculated nitrogen content, assuming that crosslinking occurred quantitatively in accordance with Reaction 3 (neglecting auxiliary step 5) is 0.18 per cent. While this reasonably good agreement may be fortuitous, there can be little question that the vulcanizate contained approximately the expected quantity of combined nitrogen.

Extractable Quinone Dioxime.—From the concentrated extracts it was possible to isolate two products: (1) a fraction of a gram of highly insoluble brown powder that was not identified, and (2) a light brown powder that was recrystallized from methylethyl ketone to yield about 0.8 gram of light colored crystals, soluble in alkali with the intense dark coloration suggestive of quinone dioxime and having the following composition: C: 53.38, 53.18; H, 4.52, 4.50; N, 19.92, 19.71 (quinone dioxime, C, 52.17; H, 4.38; N, 20.29). Oxidation of the second product with fuming nitric acid[20] yielded some prismatic crystals, which were recrystallized from hot alcohol to give pale yellow crystals of *p*-dinitrobenzene: melting point 173–174° C (corrected); mixing melting point with Eastman reagent 173–174° (corrected); literature value 173.5–174°. These crystals reacted with naphthalene in warm alcohol to form fine white needles of the addition product, $C_{10}H_8 \cdot C_6H_4(NO_2)_2$. These results indicate that quinone dioxime is formed in the vulcanization of Butyl rubber with *p*-dinitrosobenzene.

According to the theory outlined above, one would expect dinitroso compounds to display vulcanizing activity in natural as well as in other synthetic rubbers. Table V shows that natural rubber, Buna-S, Buna-N, and Neoprene can be vulcanized by means of *p*-dinitrosobenzene[21].

DISCUSSION OF VULCANIZATION

According to the theory of vulcanization of Butyl by quinone dioxime in the presence of oxidizing agents, the active agent is the dinitroso compound formed

TABLE V

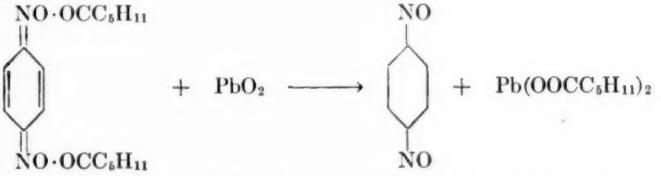
VULCANIZING ACTIVITY OF DINITROSO COMPOUNDS IN NATURAL AND SYNTHETIC RUBBERS

	Natural Rubber[a]			Buna-S[b]			Buna-N[c]			Neoprene-GN[d]		
Cure at 142° C (min.)	15	30	60	15	30	60	15	30	60	15	30	60
Tensile strength (lb./sq. in.)	870	850	900	1330	1130	1270	1580	1790	1600	3450	3380	2950
Ultimate elongation (%)	360	320	320	490	450	450	500	480	420	255	285	200

[a] Smoked sheet 100, stearic acid 3, zinc oxide 5, channel carbon black 50, *p*-dinitrosobenzene 1.
[b] Buna-S 100, stearic acid 1.5, zinc oxide 5, channel carbon black 50, *p*-dinitrosobenzene 1.
[c] Buna-N 100, stearic acid 1.5, zinc oxide 5, channel carbon black 50, *p*-dinitrosobenzene 1.
[d] Neoprene-GN 100, stearic acid 1, zinc oxide 1, channel carbon black 60, p-dinitrosobenzene 1.

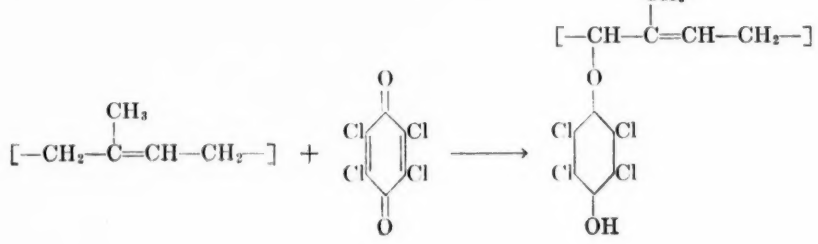
by oxidation of the dioxime. An oxidation-reduction reaction then takes place in which isoprene units in adjacent chains are finally linked together, and quinone dioxime is formed as a reaction product. This scheme conforms to the general oxidation-reduction mechanism proposed by Fisher[3] for natural rubber vulcanization, with the essential differences that the hydrocarbon double bond probably reacts with the vulcanizing agent in its higher state of oxidation, and that no nonrubber components are present, or need be invoked, to bring about the reduction step. A further fundamental difference between our views and those of Fisher should be emphasized. Regardless of the oxidations and reductions which may occur during vulcanization, these are only incidental to the essential process which is one of cross-linking of rubber molecules.

The authors consider that the same types of reaction are responsible for the vulcanization of Butyl by some derivatives of dioximes, such as their esters, when oxidizing agents are present. For example, the first step in the vulcanization of Butyl by quinone dioxime dicaproate and lead dioxide is believed to be given by:



Evidence for this view was found in an experiment in which quinone dioxime dicaproate was reacted with lead dioxide in boiling xylene. Lead dicaproate was isolated from the reaction mixture and identified. The amount of lead dioxide consumed in the reaction was in approximate agreement with the equation. The reactions following the formation of the dinitroso compound are presumably the same as those already indicated.

When natural rubber is vulcanized with halogenated quinones—*e.g.*, tetrachloroquinone—especially in the presence of an oxidizing agent[3], some of the corresponding hydroquinone is formed and is then oxidized to the original quinone. Farmer[22] considers that this proceeds according to the reaction:



It is followed by dehydrogenation of the α-methylenic carbon from the adjacent CH_2 group of the next isoprene unit to produce a conjugated diene structure that may lead to cyclization or cross-linking. He presents the alternative possibility, however, that the quinone may serve to some extent as an oxidation-reduction system and thus lead to a more direct radical linking of the rubber chains:

$$2\left(\rangle C_5H_8\right) + QCl_4 \longrightarrow 2\left(\rangle C_5H_7^{\bullet}\right) + H_2QCl_4$$

$$2\left(\rangle C_5H_7^{\bullet}\right) \longrightarrow \rangle C_5H_7 \cdot C_5H_7 \langle$$

It seems unlikely that either of these two mechanisms can be proposed for the analogous case of vulcanization of Butyl rubber by quinone dioxime in the presence of an oxidizing agent, since the reactions suggested by Farmer would both result in vulcanization through carbon-to-carbon cross-linking and would not explain the presence of combined nitrogen in the Butyl vulcanizate. The first mechanism, furthermore, is ruled out by the fact that, unlike those occurring in natural rubber, the isoprene units in Butyl molecules do not form sequences[8].

In view of the pronounced activity of dinitroso compounds in vulcanizing Butyl, the principal rate-determining reaction would appear to be the initial oxidation of the dioxime. This rate would be expected to depend on the number and kind of substituent groups introduced into the latter compound, and could account for the wide range of activities observed in these laboratories[4] with various derivatives of dioximes. If, however, the second step in the vulcanization reaction takes place as indicated in step 2, especially when the dinitroso compound is the starting material, the observed rate would depend on the particular dinitroso compound formed, provided the latter exists, as suggested, in hydrocarbon media as an equilibrium mixture of the monomolecular and bimolecular species. The latter premise seems to be reasonable, in view of the chemical evidence previously discussed. In this connection it is of interest to point out that, when equimolar concentrations of nitrosobenzene, on the one hand, and of *o*-nitronitrosobenzene, on the other, are allowed to react with Butyl in benzene solution, the apparent rate of reaction is considerably greater with the ortho derivative[23]. According to Hammick[15], in benzene solutions of these two substances at the freezing point, nitrosobenzene is only about 2.5 per cent associated, whereas *o*-nitronitrosobenzene is about 78 per cent associated.

Wright and Davies[24] found that polynitrobenzene vulcanization of natural rubber is effective with highly purified rubber only in the presence of basic oxides, such as litharge or barium oxide, and water. They noted that these are the exact conditions required for the decomposition of *m*-dinitrobenzene into oxalic acid, carbon dioxide, and ammonia, on the one hand, and into reduction products which were inferred from oxygen and nitrogen analyses to have a mean state of reduction represented by 3,3′-dinitroazoxybenzene. They found, nevertheless, that none of the reaction products or products such as azo or azoxy compounds inferred to be present, exhibited vulcanizing activity. Their analytical data point, with apparently equal plausibility, to the reduction products which have a mean state of reduction represented by dinitrosobenzene.

In view of the preceding data and discussion it is possible to present an alternative hypothesis for vulcanization by polynitro compounds. According

to this view, some of the nitro compound is reduced to the nitroso state either by nonrubber components or by the basic oxide. In this connection, when nitrobenzene is heated with barium oxide or iron powder, some nitrosobenzene is formed[25]. In the absence of rubber, some of the nitroso compound is further reduced to the phenylhydroxylamine. This reacts with the nitrosobenzene derivative to give an azoxy compound according to the scheme:

$$ArNO_2 \xrightarrow{-O} ArNO \xrightarrow{H} ArNHOH \xrightarrow{ArNO} ArN{=}\underset{O}{N}Ar + H_2O$$

In the presence of rubber the nitroso derivative reacts readily with the rubber, as observed by Bruni and Geiger in the case of nitrosobenzene, without undergoing further reduction. Similar reaction of another nitro group of the polynitro compound with a neighboring rubber chain produces cross linkage and thus effects vulcanization. This hypothesis will account for the observation made by Fisher and Gray[26] that the unsaturation during vulcanization by polynitro compounds remains unchanged; Bruni and Geiger showed that the addition of nitrosobenzene to rubber involves no net consumption of carbon-to-carbon unsaturation. If the same type of condensation occurs with the polynitroso compound, which we have considered to be formed from the polynitro compound, no change in unsaturation should be expected[27].

The foregoing hypothesis resembles only superficially one proposed by Ostromislensky[28], who attempted to prove that polynitrobenzene vulcanization entails transfer of oxygen to the rubber:

$$ArNO_2 \longrightarrow ArNO + O$$

His observation, however, that neither nitrosobenzene nor isonitrosocamphor is an effective vulcanizing agent is irrelevant, since both of these substances are monofunctional and are therefore incapable of directly joining two rubber chains.

SUMMARY

Experiments have been carried out to determine the chemical reactions that occur when Butyl rubber is vulcanized by quinone dioxime or related compounds. Observations have been made of the reactions of these substances with simple olefins, and of the effect of oxidizing agents on the dioxime-type of vulcanization of Butyl in solution. The theory is proposed that, in the vulcanization of Butyl by quinone dioxime or its esters, in presence of oxidizing agents, the active agent is *p*-dinitrosobenzene formed by oxidation of the dioxime. Chemical reactions are suggested for the subsequent cross-linking or vulcanizing steps, and the results of confirmatory experiments are presented. *p*-Dinitrosobenzene and other polynitroso compounds are active vulcanizing agents for Butyl, natural rubber, Buna-S, Buna-N, and Neoprene, and do not require the addition of an oxidizing agent. It is suggested that vulcanization of natural rubber by polynitro compounds involves their reduction to corresponding nitroso compounds as the first step, and that the nitroso group adds to rubber to produce cross-linkages.

ACKNOWLEDGMENT

The authors are grateful to S. B. Lippincott for synthesizing some of the reagents used in this study, to John A. Thomas for assisting in the experimental work, and to their colleagues who carried out the compounding and evaluation

work, and with whom they had the opportunity of discussing some phases of the problem. They are also indebted to Harry L. Fisher for helpful criticism of the manuscript.

REFERENCES

[1] Ostromislensky, *J. Russ. Phys.-Chem. Soc.* **44**, 204 (1912).
[2] Ostromislensky, in "The Chemistry and Technology of Rubber," edited by Davis and Blake, Reinhold Publishing Corp., New York, **1937**, p. 274.
[3] Fisher, *Ind. Eng. Chem.* **31**, 1381 (1939); RUBBER CHEM. TECH. **13**, 50 (1940); U. S. patents 1,918,328 (1933); 2,170,191 (1939).
[4] Haworth, J. P., to be published.
[5] Thomas and Sparks, Australian patent 112,875 (1941).
[6] Thomas, Sparks, Frolich, Otto and Mueller-Cunradi, *J. Am. Chem. Soc.* **62**, 276 (1940).
[7] Brill and Halle, *Naturwissenschaften* **26**, 12 (1938); Fuller, Frosch, and Pape, *J. Am. Chem. Soc.* **62**, 1905 (1940); RUBBER CHEM. TECH. **14**, 338 (1941).
[8] Rehner, *Ind. Eng. Chem.* **36**, 46 (1944); RUBBER CHEM. TECH. **17**, 346 (1944).
[9] Nietzki and Kehrmann, *Ber.* **20**, 613 (1887).
[10] Forster and Barker, *J. Chem. Soc.* **103**, 1918 (1913); Hammick, Edwardes and Steiner, *J. Chem. Soc.* **1931**, p. 3308; Tappi and Demorra, *Gazz. chim. ital.* **69**, 708 (1939).
[11] Kostanecki, *Ber.* **20**, 3133 (1887).
[12] Forster and Fierz, *J. Chem. Soc.* **91**, 1942 (1907).
[13] Sidgwick, "Organic Chemistry of Nitrogen," Oxford Univ. Press, London, **1937**, Chap. 7.
[14] Ruggli and Petitjean, *Helv. Chim. Acta.* **21**, 711 (1938).
[15] Hammick, *J. Chem. Soc.* **1931**, 0. 3105.
[16] Kehrmann and Messinger, *Ber.* **23**, 3557 (1890).
[17] Angeli, Alessandri and Pegna, *Atti accad. Lincei* [5] **19**, 650 (1910); Alessandri, *Gazz. chim. ital.* **51**, 125 (1921); **54**, 426 (1924).
[18] Burkhardt, Lapworth and Walken, *J. Chem. Soc.* **127**, 1742, 2458 (1925).
[19] Alessandri, Atti accad. Lencei [5] **24**, 62 (1915); *Gazz. chim. ital*, **54**, 426 (1924); Bruni and Geiger, *Atti accad. Lincei* (6) **5**, 823 (1927); RUBBER CHEM. TECH. **1**, 177 (1928); Pummerer and Gündel, *Ber.* **61**, 1591 (1928); RUBBER CHEM. TECH. **2**, 373 (1929).
[20] Nietzki and Kehrmann, *Ber.* **20**, 613 (1887); Nietzki and Guiterman, *Ber.* **21**, 428 (1888).
[21] Rehner and Flory, patents applied for. A commercial vulcanizing agent, Polyac, which has recently become available, contains *p*-dinitrosobenzene as the active ingredient. Some properties of Butyl vulcanizates prepared with this product have been published by Sturgis and Trepagnier (*Rubber Age* (N.Y.) **54**, 325 (1944)).
[22] Farmer, *Trans. Faraday Soc.* **38**, 340 (1942); RUBBER CHEM. TECH. **15**, 765 (1942); **16**, 769 (1943).
[23] Rehner, John, Jr., unpublished results.
[24] Wright and Davies, *Trans. Inst. Rubber Ind.* **13**, 251 (1937); RUBBER CHEM. TECH. **11**, 319 (1938).
[25] Zerewitinoff and Ostromislensky, *Ber.* **44**, 2402 (1911); Rinkes, *Chem. Weekblad* **11**, 1062 (1915); *Chem. Zentr.* **1915**, I, 251.
[26] Fisher and Gray, *Ind. Eng. Chem.* **20**, 294 (1928); RUBBER CHEM. TECH. **1**, 101 (1928).
[27] These views appear to be inconsistent with the results of Blake and Bruce (*Ind. Eng. Chem.* **29**, 866 (1937), who concluded that double bonds in natural rubber are consumed during vulcanization by polynitro compounds. However, these authors based their conclusions in part on the observation that the polynitro compounds which they employed were inert toward Wijs reagent. They were presumably unaware of the fact (see Reference 23) that aromatic nitroso groups, the formation of which we propose in our hypothesis, react readily with Wijs reagent. Also one of us (see Reference 23) observed that, in the reaction of an olefin such as 2-methyl-2-butene with Wijs reagent, the total uptake of halogen under certain conditions is markedly reduced when a few per cent of a compound such as *p*-nitrosodimethylaniline is added to the olefin. These results suggest that the apparent consumption of rubber double bonds observed by Blake and Bruce may not be real. In the event that their conclusions prove correct, our hypothesis for vulcanization by polynitro compounds would require revision.
[28] Ostromislensky, *J. Russ. Phys.-Chem. Soc.* **47**, 1453 (1915).

EVALUATION OF THE PHYSICAL PROPERTIES OF RUBBER VULCANIZATES AT LOW TEMPERATURES *

L. MULLINS

Introduction.—The technical importance of rubber vulcanizates in fields where they are likely to be subjected to temperatures lower than normal requires no emphasis, and has resulted in considerable activity being directed to the evaluation of the physical properties of rubber vulcanizates at such temperatures. The purpose of these investigations has been to compare the low temperature serviceability of various rubbers, and to study of the behavior of the materials at these temperatures in order that the data obtained may be used to assist design. Such extension of knowledge is of great importance since rubber vulcanizates exhibit considerably increased stiffness and become brittle at low temperatures. Several good summaries of the work exist in the literature[1]; these show that there is a considerable lack of uniformity in the methods of testing and representation.

As a result of this wide diversity of test methods, there is no generally accepted index of low-temperature serviceability. Many of the tests which have been used involve the extension of the usual technical tests to lower temperatures, whereas others involve a study of the performance of rubber components in conditions of service. The results of such tests generally have been quoted as a temperature below which a particular property fails to fulfil a given requirement. The endeavor to obtain one temperature or one parameter which characterizes the resistance to low temperatures has been only partially successful, since the interdependence of stress, strain, time and temperature make it impossible to formulate relations of a simple character which describe the behavior of rubber vulcanizates over even a limited range of conditions.

First, there is the need for an accepted standard test (or tests); secondly there is the need for a convenient method of expressing the resistance to low temperatures, and lastly, there is the need for the development of the ideas of the processes leading to the changes in physical properties at low temperatures. In this paper it is intended to review the various methods which have been suggested for low-temperature testing, to indicate the sources of the inadequacy of the individual tests, and to describe the initial results of an investigation, as yet incomplete, into a convenient means of testing and representing the mechanical properties at low temperatures.

Types of Test Methods.—In the investigation of the low-temperature behavior of rubber three distinct types of test methods have been employed.

(1) The determination of the temperature at which rubber fractures suddenly, without preliminary stretching, under an increase in load. This is referred to as the brittle point, or brittle temperature, and it indicates the temperature at which rubber would fail structurally under the given conditions

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 21, No. 4, pages 247–266, December 1945.

of loading. This temperature is usually well defined, although it has a pronounced dependence on the magnitude and rate of application of the stress.

(2) The second method involves the determination of the temperature at which a physical property shows a definite discontinuity. However, the physical property showing such a transition, *e.g.*, coefficient of expansion, latent heat, specific heat, is generally not of immediate interest in the application in service. Although this method may not indicate the temperature at which the rubber loses its serviceability, it has been shown that these transition temperatures indicate a change in structure which corresponds to internal hardening and thus represents the temperature limitations of the rubber compound. This method may be the most powerful in the provision of data to develop ideas of the mechanisms responsible for the change of physical properties with temperature.

(3) The last method evaluates a temperature at which at least one of the rubberlike properties changes adversely to such an extent that the rubber component ceases to fulfil its function. To obtain a reliable indication of low-temperature serviceability, tests of this type must be employed. The value of the temperature obtained from tests of this type depends on the property chosen, but in general it is higher than that given by the two previous types.

It is significant that the results of all these methods fall within a limited range of temperatures for any one material, despite the fact that tests of types (1) and (3) are necessarily defined in an arbitrary way. It has been shown recently[2] that this is not fortuitous, but results from a fundamental similarity between the processes measured.

In the following sections the various tests of each type are surveyed in detail, and the interpretation of the more valuable tests discussed.

Brittle Point Tests.—A comprehensive survey of the various methods used in determining the brittle point has been given by Graves and Davies. The brittle point is the temperature at which fracture or cracking occurs when standard test-pieces are exposed to the specified low temperature for definite periods and are then bent through a fixed angle at a reproducible high rate of deformation. As Kemp, Malm and Winspear[3] demonstrated that the sharply defined brittle point was lowered when the speed of application, or magnitude of the stress was reduced (in both cases the rate of straining is reduced), it has been recognized that all variables in the test must be carefully controlled, so that either (i) comparative results of the utility of a series of rubber compounds are obtained, or (ii) the results indicate the performance to be expected in the conditions of service. The change in brittle point with conditions of test varies considerably with various types of rubber vulcanizates, and for some synthetics a change of more than 25° C has been reported by Winspear[4] under various conditions of test. The present tentative American Society for Testing Materials method of testing merely specifies that the deformation should be carried out as rapidly as possible, this lack of precision is undesirable and capable of producing misleading results.

Although the brittle point indicates when the flexibility of the rubber vulcanizate ceases and when the sample can no longer withstand a severe mechanical deformation without fracture, it gives no information about the gradual stiffening as the temperature is lowered, or the loss of serviceability on cooling, *e.g.*, it is possible to have a vulcanizate with a low brittle point and yet too stiff for general use at much higher temperatures. For some specific applications data on the brittle point may be the only information required, *e.g.*,

rubber cable covers or rubber tubing. But generally data on rubberlike properties, such as hysteresis and stiffness, are required over the temperature range likely to be encountered in service before the user is in a position to make a selection from a series of vulcanizates.

Transition Point Tests.—A considerable amount of work has recently been performed investigating socalled second-order transitions of high polymers. It has been observed that many physical properties of rubberlike compounds exhibit marked changes when the compound is heated or cooled through a small range of temperatures. Bekkedahl and his coworkers[5] have been responsible for much elegant experimental work in this field. They have observed second-order transition points in the changes of the following properties with temperature:—linear dimensions, coefficient of expansion, density, thermal capacity, specific heat, entropy and enthalpy; the measurements being made on natural rubber and various synthetics.

Electrical measurements have shown discontinuities at similar temperatures and Davies, Miller and Busse[6] have demonstrated a relation between these properties and changes in hardness with temperature. All the transition points determined from discontinuities of the various thermal, mechanical, electrical, and optical properties show great similarity. These transitions are quite distinct from crystallization as in many cases no sudden structural changes are observed by x-ray studies. However, it has been noticed by Rands, Ferguson and Prather[7] that the transition temperature depends on the rate of change of temperature with time; this will be mentioned again later when discussing the conditioning of samples prior to testing.

Recently several workers[8] in this field have stressed the strict similarity between the fundamental mechanisms which are involved in all these processes, *i.e.*, the energy associated with orientation of the molecular segments of the long rubber molecular chain. Alfrey, Goldfinger and Mark suggest that the transition temperature as normally measured does not represent a fundamental property, but is the temperature at which the rate of molecular rearrangement is of the same order as the time scale of the experiment. This agrees with the observations of Rands, Ferguson and Prather recorded above. Below the true transition point the individual molecular segments do not carry out rotational movements and so the rubber is brittle; above the transition point the number of degrees of freedom of the segments increase and they carry out rotational and vibrational movements associated with rubberlike properties.

The temperatures of the transition points are obviously as yet of limited value as an index of low temperature behavior, and have no application in general practice, but knowledge of their behavior has already assisted in simplifying the complex problem of conditioning of samples.

Tests Involving Modulus or Deformation: Time Measurements.—Numerous tests of the third type have been described. Historically, the approach has been the extension of standard tensile or other tests to low temperatures. Although there is little new in the test methods, some confusion exists as to the interpretation and adequacy of the results. In this paper, for the reasons already advanced, we are mainly interested in tests of this type.

In many of the tests employed the change of modulus of elasticity in tension, shear, or compression is observed as the temperature is progressively decreased. The observed value of the modulus depends on the period of deformation, and any future reference to the term modulus will implicitly involve the period during which deformation takes place. Such tests are of obvious importance, since the modulus governs the behavior of rubber vulcanizates in

numerous conditions of service, *e.g.*, vibration absorbers, in such cases a limiting high value of the modulus can be quoted, and the temperature below which the vulcanizates exceed the limit of stiffness permitted by service can be used as the low temperature index. Other tests involve the measurement of the change of deformation with both time and temperature. It is this time dependence of the deformation which is characteristic of all rubberlike properties, and is the source of the relation between recovery properties, hysteresis and energy absorption, and the resistance to physical deformations (modulus).

It is appropriate that this relationship should be discussed so that it may be used in a discussion of the adequacy of the conventional methods of testing and ways of expressing results. The following analysis is based on simplifying assumptions, but it is considered possible to draw general conclusions from it, even if the behavior of rubber compounds is more complex.

In considering the effect of changes of temperature and time on the deformation of rubber compounds, Aleksandrov and Lazurkin[36] have shown that to a first approximation the deformation $d(t)$ attained after a time t may be expressed by the relation:

$$d(t) = d_{oe} + d_{he}(\infty)(1 - e^{-t/\tau})$$

where d_{oe} is the true-elastic component of the deformation, it is reversible and is independent of the time t (acoustical or instantaneous deformation). D_{he} is the high-elastic component of the deformation, which is reversible but dependent on time and reaches $(1 - 1/e)$ of its final value $d^{he}(\infty)$ in a time t equal to τ. The time constant τ is related to the rotation of the molecular segments which are associated with the high-elastic component of deformation. As the rotation of the molecular segments can be represented only by a distribution of values of orientation times, it is questionable whether the value of τ is more than a curve-fitting parameter.

In developing this analysis Eley[9] and Tuckett[10] had added a viscous component d_{visc} to the deformation represented by the right-hand side of the equation. This represents irreversible viscous flow. However, at low temperatures this component is extremely small and can be neglected. The true-elastic component is also small and is practically independent of temperature. Thus the high-elastic component has by far the greatest influence on the change of deformation with time and temperature, this dependence being controlled by the value of the time constant τ. The value of τ increases as the temperature is lowered, and as a result the rubber compound takes a longer time to attain a particular deformation. It is important to note that a similar final deformation is reached at low as at high temperatures, but at lower temperatures the deformation is reached more slowly. Here it is assumed that the temperature dependence of the term $d_{he}(\infty)$ is extremely small compared with the temperature dependence of τ.

Modulus Tests.—The many modulus tests which have been described show a variety of experimental technique. The change of the modulus with temperature has been measured in extension, compression, bending, and torsion. The results from all modulus tests are of the same characteristic form, and as a torsion modulus test is used at the R.A.B.R.M. laboratories, the results of torsion tests will be used to illustrate the following discussion of the ways of interpreting results.

The apparatus which is used at the R.A.B.R.M. to determine the change of modulus with temperature is similar to that used by Church and Daynes[11] in their measurements on the plastic yield of ebonites (Figure 1). The experi-

mental procedure which is adopted is to determine the deflection of the mirror produced by a known torque in 20 seconds; the torque is initially adjusted so that at room temperatures the angular deflection is about 10 degrees; the samples used are 9.5 cm. long, 1.5 cm. wide and 0.5 cm. thick. Other workers in this field who have measured torsion modulus include Yerzley and Fraser[12], Clash and Berg[13] Imperial Chemical Industries, Ltd.[14], and Bilmes[15]. The simplest methods of testing involve either the observation of the deformation produced by a constant load during equal periods of time, or the observation of the load which produces a constant deformation in a given time, or the observation of the time taken to produce a constant deformation with a constant load. From the first two sets of observations values of the apparent modulus can be calculated; from the last set information of the time dependence of the deformation is obtained.

The necessity for an understanding of the mechanisms involved before devising a new method of test is well illustrated by a survey of the various modulus tests. A lack of appreciation that the measured value of the modulus depended

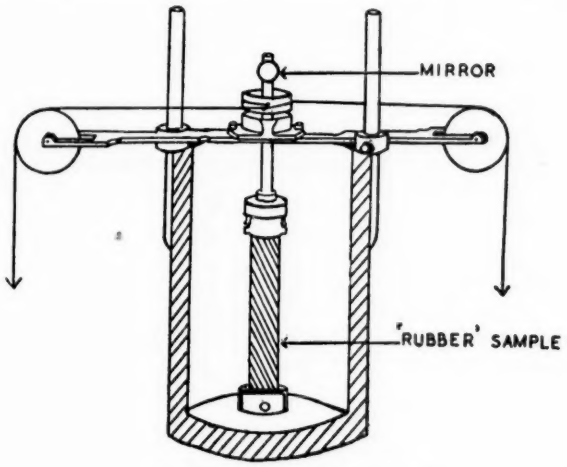


FIG. 1.—Torsion modulus apparatus.

on the time taken to produce the deformation led Yerzley and Fraser to discard their torsion modulus test; Koch[16] and Kish[17] measured deformations which implicitly involved time effects which were not carefully controlled. Liska[18], although recognizing the need for control of time of deformation, did not design his experiments with full regard to its significance. As a consequence, results even if reproducible cannot be used with confidence to describe the low temperature behavior of rubber compounds.

Clash and Berg,[13], and the Imperial Chemical Industries (Dyestuffs)[14] recorded, respectively, the angle of twist produced by a known torque in five seconds, and the torque required to produce a given angular twist in five seconds, and were thus the first to publish the design of low-temperature tests with adequate time control. Somerville[19] and Graves and Davies[20] measured the low temperature modulus on a Scott tensile-test machine; and Morris, James and Evans[21] measured the elongation produced by a known load in three minutes. The recently proposed tentative A.S.T.M. method of test for stiffen-

ing at low temperatures is similar to that due to Liska except that it does not possess the deficiencies resulting from an inadequate control of time. In this proposed test the deflection of a beam subjected to a given load is observed after 15 seconds, loading, and a curve of Young's Modulus against temperature is derived. While this paper was in preparation, Conant and Liska[22] published a paper in which they describe a similar modulus test which shows full regard for the time dependence of the deformation; another aspect treated in this paper will be referred to later.

Characteristic curves obtained using the torsion apparatus are shown in Figure 2. Here the modulus is plotted on a logarithmic scale as a function

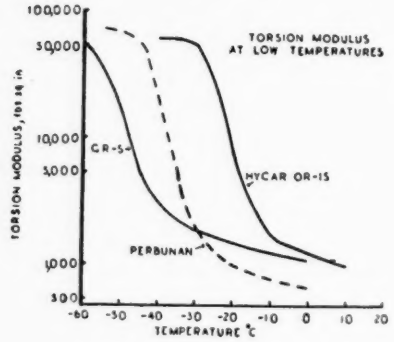


FIG. 2.

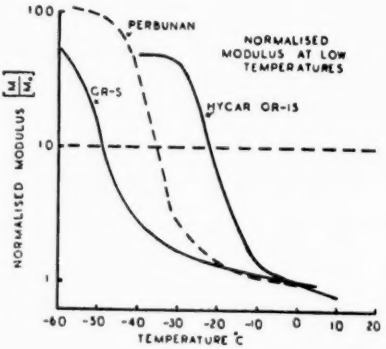


FIG. 3.

of the temperature, the value being calculated from observations of the deformation produced by a constant load in equal intervals of time (20 seconds) using the following approximate formula which involves the dimensions of the sample and the torque.

$$\text{Rigidity Modulus} = \frac{tl}{ab^3\mu\phi}$$

where

t is the torque applied to the specimen
l is the specimen length
a is the specimen width
b is the specimen thickness
ϕ is the angle of twist
μ is a function of b/a

The value of μ can be obtained from tables[14]. This formula is only approximate, but this is not considered a serious drawback since it is the change of stiffness which is of greater interest, and for many purposes curves showing the change of the reciprocal of the deformation, which is proportional to the modulus, are adequate. It was found experimentally that the shape of these modulus temperature curves was independent of the applied torque within the accuracy of measurement.

These curves show that, at the higher temperatures, the deformation is large; this corresponds to a more or less complete attainment of equilibrium by the high elastic component of deformation; at intermediate temperatures the high elastic component of deformation takes a longer time to reach its

equilibrium state and, as a result, the deformation produced in 20 seconds is smaller. At still lower temperatures there is a rapid decrease in the 20-second deformation to a limiting value which corresponds to the true elastic component, as here the contribution of the high elastic component is extremely small. If the period of deformation is either longer or shorter than 20 seconds, then the measured value of the modulus is respectively smaller or larger than the 20 seconds value. At low temperatures, however, all measured values of the modulus approach a constant value which corresponds to the true elastic deformation. Thus the shape and position of the modulus curves are altered by changes in the period of deformation; these changes are comparatively small for the possible changes in period which can be conveniently used in laboratory experiments, *i.e.*, a few seconds to several minutes.

In order that comparisons can readily be made it is desirable that the elastic properties should be described in terms of a few simple parameters, and here a compromise has to be made. The normal practices are to quote either the temperature at which the modulus reaches a limiting high value, or the temperature at which the modulus is an arbitrary number of times the modulus at some specified temperature. Both these procedures possess similarities as the modulus at normal temperatures is known. In the past it has been the practice at the R.A.B.R.M. to publish the temperature at which the modulus is ten times its value at 0° C. A similar practice has also been recommended in the Services Rubber Investigation[14]; such temperatures will be referred to in future as the stiffening points. Figure 3 shows curves of similarly compounded synthetic rubber mixings where the normalized modulus, or the ratio of the modulus to its value at 0° C, is plotted, again on a logarithmic scale, against temperature. It is considered that stiffening points defined in this way are of more value than those derived from a limiting high value of the modulus, since this high value of the modulus will vary considerably for different service applications. Changes in the period of deformation from 2.0 to 5 and from 20 to 120 seconds resulted in changes in the stiffening point of only ±2° or 3° Centigrade.

For most rubber vulcanizates the value of the stiffening point corresponds to the temperature at which the slope of the logarithm of the modulus against temperature is a maximum, *i.e.*, the mid-point of the steeply rising straight portion of the curve.

However, stiffening points do not give any indication whether stiffening takes place suddenly, as the temperature is decreased, at temperatures near the quoted value, or whether it takes place gradually over a wide range of temperatures. Figure 4 shows the normalized modulus curves obtained for two rubber compounds, and illustrates this feature. The plasticized Neoprene-GN compound shows a lower stiffening point, yet over a considerable portion of the range of temperatures from 0° C to its stiffening point it shows more stiffening than the Perbunan compound. Another difficulty which ensues from defining stiffening points in this way occurs when the compounds show this rapid stiffening, with decrease in temperature, at temperatures higher than 0° C. Fortunately few rubber compounds exhibit this effect, but in the cases where it exists, the value the modulus would have had at 0° C if rapid stiffening had not taken place is used as a basis for normalized modulus calculations. This is illustrated in Figure 5; the Hycar OR-5 vulcanizate shows rapid stiffening at temperatures below 30° C, but at temperatures above 40° C the rate of change of logarithm of the modulus with temperature is small and is approximately constant; this rate of change has been used to determine the

value that the modulus would have had in the absence of rapid stiffening; *i.e.*, the Hycar OR-5 curve above 40° C has been produced with a dotted line to lower temperatures. In Figure 5 the modulus curves have been normalized, and the position of the curves adjusted so that the dotted line passes through a normalized modulus value of 1 at 0° C. Thus the stiffening point for the Hycar OR-5 vulcanizate is indicated in Figure 5 by the temperature at which the normalized modulus is 10. Such a procedure has many drawbacks, and has not been adopted in the final recommendations

Other authors[23] have defined the stiffening point as the temperature at which the modulus starts to increase rapidly, but Figure 4 indicates that such a definition can have little general application and that for many compounds it will be impossible to determine such a temperature.

Other tests which can be classified with modulus tests are those in which the change of hardness with temperature is recorded, an increase in modulus resulting in an increase in hardness. Scott[24] has shown that for hardness tests

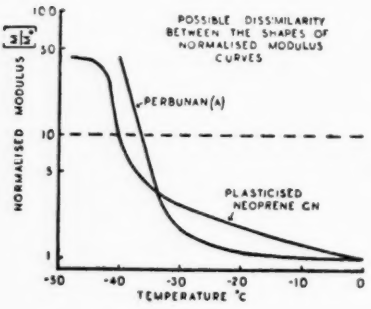


FIG. 4.

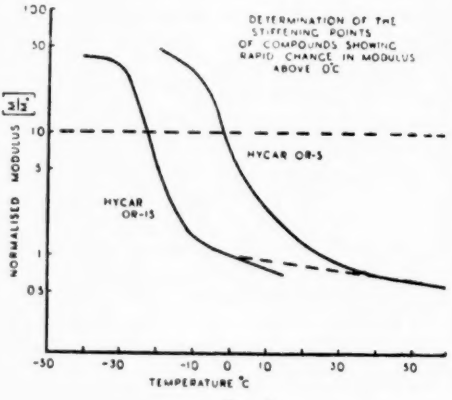


FIG. 5.

in which a spherical indentor is used, the following relationship exists between the modulus e and the depth of indentation h:

$$e = \frac{a}{h^{1.35}}$$

Where a is a constant involving the radius of the indentor and the load.

Yerzley and Fraser[12] described a simple test in which the change in Shore durometer hardness was measured, and they defined a freezing factor to assist in the comparison of results. The freezing factor at any temperature is the ratio of the actual increase in hardness to the maximum possible increase in hardness, *i.e.*, to 100 Shore units.

$$\text{Freezing factor} = \frac{\text{hardness at low temperature—hardness at room temperature}}{\text{100—hardness at room temperature}}$$

Although such a test is apparently simple, there are experimental difficulties involved at low temperatures; dew condenses inside the hardness gauge and causes sluggishness and inaccuracies; furthermore the value of hardness at low temperature is difficult to assess, as the indentation gradually increases with time. As in the modulus experiments it is essential to measure the hardness

after a definite interval of time, but Yerzley and Fraser do not appear to have considered this precaution.

Tests Involving Deformation-Time Measurements.—Although measurements of the time dependence of the attainment or recovery of deformation seem to provide the simplest means of investigating the change of properties with temperature, little constructive work of this nature has been done on low-temperature tests. The tests which have been performed have been complex and difficult to analyze. Further, in general, they do not give any precise indication of the behavior likely to be encountered in service, and as a result have not achieved any great popularity.

Le Blanc and Kröger[25]; Sagajllo, Bobinska and Saganowski[26]; and Morris, James and Evans[27]; have described experiments in which they measured the set remaining a given period after removing the stress on a stretched sample. Graphs of set plotted against temperature are complementary to the graphs of deformation against temperature which have already been discussed, and indicate a slowing-up of the rate of the high-elastic component of the deformation as the temperature is decreased.

Similar experiments performed on ebonite at elevated temperatures have been reported by Church and Daynes[37], who measured both the residual deformation remaining after a definite period of recovery of a sample which had been subjected to a fixed torsional strain for a controlled period, and the rate of change of the deformation of a sample subjected to a fixed stress. Such experiments could be used also in low-temperature tests. In a subsequent paper[11] they describe developments of the apparatus, and indicate that experiments performed under conditions of fixed stress are the more valuable.

In experiments performed with a fixed initial strain, they obtained curves of the residual deformation (after 2 minutes' recovery and expressed as a percentage of the initial deformation) against temperature. These curves showed a sharp maximum at a temperature characteristic of the material. Changes of the conditions of the test somewhat altered the shape of the curves, but caused little alteration in the value of the peak-temperature. Results of experiments in which the strain is fixed cannot be easily interpreted as with changes in temperature the relative magnitudes of the high-elastic and true elastic components of deformation change[29]. Deflection-temperature curves obtained from experiments at constant stress were similar to the curves shown in Figure 2, they suggested that a convenient temperature for reference purposes was the intercept of the rising straight portion of the curve on the temperature axis. Owing to the considerable dissimilarity between the shapes of the modulus-temperature curves obtained at low temperatures (see Figure 4) it is considered that such a temperature could not be conveniently derived, and used as an index of low temperature serviceability.

A test which was developed to assess the state of cure of a sample and which has been used quite widely in this field is the T.50 test of Gibbons, Gerke and Tingey[30]. This test involves the cooling of a stretched sample at a temperature which is sufficient to "freeze" it, and then, on raising the temperature steadily, observing the temperature at which the sample recovers to 50 per cent of its initial elongation. McCortney and Hendrick[31] and Yerzley and Fraser[12] have attempted to use and modify this test to give results consistent with service at low temperatures. They ultimately rejected the test on the grounds of inconsistency. One source of the deficiencies of this test is that the measured value of the T.50 temperature depends on the rate of rise of temperature, and different rubber compounds may well fall into different orders of merit for

various rates of rise of temperature. Further the T.50 temperature depends on the strength of the elastic network, as well as the temperature-sensitive structure.

In studying the time dependence of deformation, or of recovery, it is well to limit the observations to a series of measurements of the change of deformation with time at various temperatures, it should then be possible to determine characteristics which are independent of the test method. Such tests will be discussed more fully in the next section.

Bilmes[15] has recently described experiments on a torsion apparatus having observed deflections produced by a constant load after various intervals of time. Graphs of the logarithm of the deflection against the logarithm of the time were obtained for samples of plasticized polyvinyl chloride; these graphs were invariably straight lines. He accounted for this behavior by applying the Nutting-Scott Blair equation:

$$\psi = s\sigma^{-1}t^{k}$$

Where ψ is the firmness of the material, and the dissipation coefficient k is a measure of the extent by which the time t influences the deformation σ produced by a stress s. He obtained values of ψ and k at various temperatures and found that k had a well defined maximum. The existence of this maximum indicates that the deformation is most time-dependent at a specific temperature. Further, he characterized four states through which the sample passed on progressive cooling, namely: plastic, rubbery, leathery and brittle, by means of ψ and k values obtained from the ψ-temperature and the k-temperature relations. Attempts to characterize the low-temperature properties of rubber compounds in this way are described in Section 6.

Experimental.—It appears that the most generally useful means of representing low temperature behavior is a complete modulus-temperature graph. This method of portraying results is obviously inconvenient, and it will be advantageous if the experimentally obtained modulus curve can be characterized by a simple expression; the work described here was undertaken with this end in view. It is reiterated, that for complete information, the time dependence of the modulus must also be known.

Two recent papers to which reference has already been made[32], have contributed to the analysis of deformation at low temperatures. Bilmes worked with plasticized polyvinyl chloride, and showed that it was possible to apply the Nutting-Scott Blair relationship to the change in deformation with time; experiments performed by the author of this paper on various rubber compounds indicate that there is fair agreement between the experimental results and the Nutting-Scott Blair power law, and confirmed Bilmes' observation that the value of k (the degree to which time affects the deformation) exhibits a maximum at a temperature similar to that obtained by stiffening point and brittle point tests. However, since both ψ and k are sensitive to changes in temperature, analysis of this type is not amenable to a simple representation of the change of properties with temperature. The value of the peak temperature gives no more evidence which is likely to be of value to the user of rubber compounds than do other stiffening-point tests.

It is possible to devise a number of expressions which represent the degree to which the deformation is a function of time, and which show a maximum value at temperatures near to the stiffening point. Conant and Liska have evaluated such an expression at various low temperatures; they observed, in

experiments performed at constant load, that the ratio of the deformation which occurred in the interval 10 seconds to 120 seconds after the application of the load, to the deformation which occurred in the whole 120 seconds, exhibited a maximum; the temperature at the maximum being somewhat higher than that derived from a modulus stiffening-point test. It is, however, difficult to assign any exact significance to the position of the maximum. A rather crude interpretation is that it is the temperature at which the sample is intermediate between the rubberlike state, with its large, rapid high-elastic deformations and snappy recovery, and the solid state, with small true elastic "crystal" deformations. The value of the temperature at the maximum, which is given by the various expressions, depends on the time scale of the experiment; as only a limited alteration of time scale is practicable in laboratory experiments of this type, the maxima of the various expressions all lie within a small temperature range.

A comment similar to that applied to the last analysis holds also for expressions of this type. Unless the expressions are simple in form or derivation, or unless they contain added data likely to be of use in service, they are of little assistance in the more complete representation of low temperature properties.

It was mentioned in an earlier section that the time dependence of the high-elastic or delayed component of the deformation was largely responsible for the change in properties with temperature, a change in temperature causing a change in the time scale of the high-elastic component. A factor τ was introduced to characterize this time dependence, and a change in temperature thus manifests itself in a change of τ. An effective solution to the problem of representing the change in modulus with both temperature and time in a convenient and adequate way would be a simple relation between both (i), the value of τ and the temperature, and (ii) the value of τ and the modulus (the modulus being determined from deformations of known duration). Knowledge of relations of this type would enable the value of modulus at any temperature to be determined with the aid of two parameters, one of which describes the temperature dependence of τ and the other describing the modulus at a known temperature.

To investigate this point, experiments were carried out to determine whether the approach of Aleksandrov and Lazurkin[36] could be applied to the results of modulus tests at low temperatures. The value of τ was measured over a range of temperatures on various rubber vulcanizates; it was obtained by measuring the time taken for the high-elastic component of the deformation under constant load to reach $(1 - 1/e)$ of its value at room temperature. The high-elastic component of the deformation was obtained by subtracting the instantaneous deformation observed at very low temperatures from all deformations. This assumes that the ordinary elastic component of the deformation is independent of temperature. In all cases considered it was found to be extremely small and could be neglected. Graphs of $\log \tau$ against the reciprocal of the absolute temperature are shown in Figure 6. It will be seen that a linear relationship exists over the limited range of temperatures considered. The range of temperatures over which values of τ can be determined simply and accurately is necessarily small. Over such short ranges of temperature a linear relationship between $\log_{10} \tau$ and the normal temperatures, *i.e.*, the temperature in ° C, not the absolute temperature, exists equally well, however the relationship:

$$\log_{10} \tau = b/t + c$$

is preferred as it is analogous to the dependence of viscosity on temperature, and hence:

$$\tau = ae^{q/rt}$$

where q/(2.3026r) is the gradient of the graph of the common logarithm of the value of τ against the reciprocal of the absolute temperature (Figure 6).

It has been suggested by Eley[9] that the value of τ can be considered to be an inverse rate constant, and that the value of q obtained from the equations above represents the energy of activation for the molecular processes which are responsible for high-elastic deformation, and corresponds to the minimum energy which molecular segments must possess before they are capable of orientation. A high energy of activation corresponds to strong bonds or restraining forces and to a rapid change of τ with temperature. The quantitative significance of energies of activation derived in this way is at present somewhat obscure, since the value of τ represents some sort of average of the orientation times of the individual molecular segments, and the width and nature of the distribu-

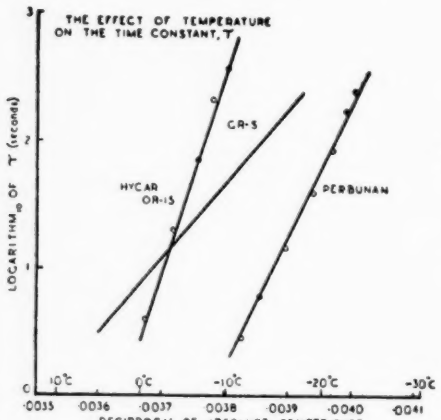


Fig. 6.

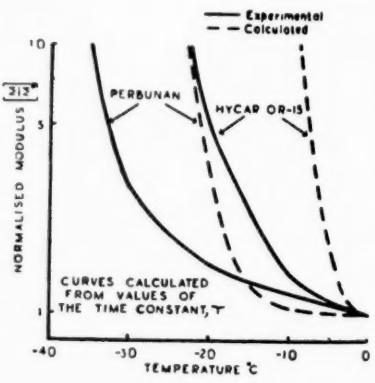


Fig. 7.

tion of orientation times of the rotating segments changes with both the temperature and the period after the commencement of the experiment.

Figure 7 shows normalized modulus curves which have been calculated for a deformation of 20 seconds duration assuming the Aleksandrov-Lazurkin relationship[36]:

$$d_{he}(20) = d_{he} \infty (1 - e^{-20/\tau})$$

These calculated values were obtained from the experimental values of the log τ against $1/t$ graph. The experimental and calculated normalized modulus curves shown in Figure 7 indicate that the Aleksandrov-Lazurkin relationship is quite inadequate over the range of temperatures where the rubber undergoes rapid stiffening. As it is in this region that agreement is required, the satisfactory representation of low temperature properties in this way demands that a simple relation between the value of τ and the modulus should be derived; such endeavors have not yet been successful.

An interesting feature of Figure 6 is that the GR-S sample has a larger value of the time constant τ, over the whole range of temperatures considered, than

the Perbunan sample, and yet it shows (see Figures 2 and 3) a considerably lower stiffening point than the Perbunan sample. A very dissimilar distribution of the orientation times of the individual molecular segments can adequately account for this behavior. A convenient way of comparing the high-elastic behavior of materials is to determine the temperature at which the value of τ is a fixed quantity. Tuckett has called such temperatures isoelastic temperatures. Apart from the fact that such temperatures can be of no more assistance in representing low temperature behavior than other critical temperatures, it appears, in view of the evidence shown in Figure 6, that such temperatures can be misleading, and that the adoption of isoelastic temperatures as a means of comparing the deformation-time behavior of materials exhibiting high elasticity involves the implicit assumption that the distribution of orientation times is similar. At least one more parameter besides τ must be introduced before an analysis of this type is capable of representing the deformation-time behavior of rubber vulcanizates, this parameter will in general show both a stress and temperature dependence.

It has been emphasized that the source of the relationship between deformation, temperature and time must be understood if a simple means of representation of low temperature properties is to be derived. However, until further fundamental investigation provides this information, it is considered that the following two parameters will be useful to describe the stiffening at low temperatures; (1) the temperature at which the modulus is twice its value at normal temperatures (20° C), and (2) the temperature at which the modulus is ten times its value at normal temperatures (20° C).

These temperatures will be referred to as t_2 and t_{10}, respectively; t_{10} is approximately the stiffening point mentioned earlier. (The reasons for selecting ratio of moduli in preference to absolute values of moduli to define these temperatures have already been advanced.) These two temperatures provide information of the degree to which the stiffening is extended along the temperature scale. Values of t_2 and t_{10} which are close together indicate rapid stiffening near the t_{10} point, whereas values of t_2 and t_{10} which are widely different indicate gradual stiffening over the range of temperatures. With the aid of these two indices an approximate normalized modulus-temperature curve can be drawn, from which it is possible to predict a value for the modulus at any temperature between 20° C and t_{10} and thus they should serve as valuable guides in practice. At temperatures lower than t_{10} the rubber compound is too stiff for most applications.

Although it is possible to draw a multitude of normalized modulus-temperature curves through the three points which are available if the t_2 and t_{10} values are known, the author considers that the discrepancies which any of the likely curves show from the observed value of the modulus will not generally be excessively large. To confirm this view, the t_2 and t_{10} values for all the synthetic rubber vulcanizates which have been used to illustrate this work, were presented to a number of people with little or no experience in the stiffening of rubber at low temperatures, and the resulting modulus curves showed in no case more than a maximum error of 25 per cent of the observed value of the modulus, throughout the range of temperature between 20° C and the t_{10} point. The shaded portion in Figure 8 shows the boundaries of the normalized modulus curves which were drawn through the t_2 and t_{10} values of three of these vulcanizates. Most of the people who were asked to assist drew curves which were much closer to the observed value of the modulus, which is shown in the figure by a full line, than the boundaries. Table 1 gives the t_2 and t_{10} values

for these vulcanizates, and also for a sample of plasticized polyvinyl chloride. This last sample together with the plasticized Neoprene-GN vulcanizate shows extreme behavior, and the boundaries of the curves drawn which satisfy their t_2t_{10} values are shown in Figure 9. Even in these cases the maximum error is still less than 25 per cent.

TABLE I

Compound	t_2	t_{10}	Stiffening point
Hycar OR-25	10° C	−5° C	−1° C
Hycar OR-15	−5° C	−20° C	−21° C
Perbunan	−18.5° C	−34° C	−35° C
GR-S	−24° C	−47.5° C	−49.5° C
Plasticized Neoprene-GN	−13° C	−40° C	−40.5° C
Plasticized polyvinyl chloride	15.5° C	5° C	9.5° C

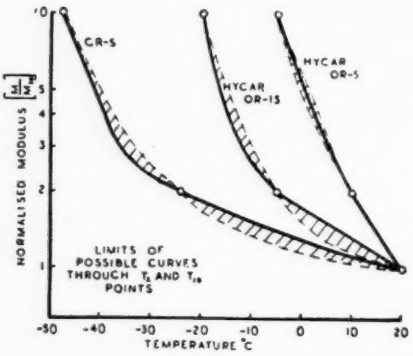


FIG. 8.

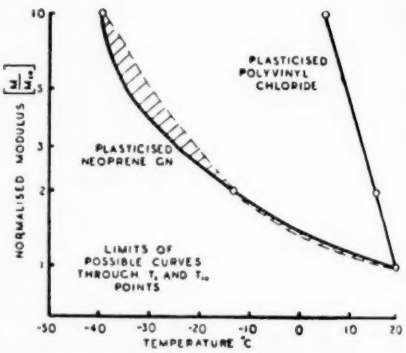


FIG. 9.

This investigation has been intentionally restricted to the change of properties at low temperature, but this suggested method of representation of the change of modulus with temperature can be easily extended to embrace the softening of materials which exhibit rubberlike properties at temperatures higher than 20° C. In these cases values of t_1 and $t_{1/10}$ can be defined respectively, as the temperatures at which the modulus is one-half, and one-tenth of its modulus at 20° C, and used to represent the softening of the material as the temperature is raised.

Changes of other Mechanical Properties with Temperature.—The mechanical property in which the user is chiefly interested is the modulus, as the majority of applications of rubbers in service are affected by stiffness and hardness. There are, however, several cases when other data besides the "static modulus" are necessary. The most important of these involve the use of rubber under conditions of repeated or rapid stressing. On such occasions the dynamic properties must be known before effective solutions to design problems can be predicted; *e.g.*, data on the resilience and the dynamic modulus is necessary for the design of shock and vibration absorbers. Little work has been reported of the measurement of the change of such properties with temperature at temperatures less than 0° C. Morran, Knapp and Linhorst[33] have described an apparatus for the measurement of the efficiency of vibration absorbers at low temperatures. In this particular application the warming of the rubber as a result of energy losses in it is important, since the mounting may be serviceable at temperatures where failure is predicted by static tests. However, they have

shown that there is a temperature below which a mounting does not warm up, no matter how long it is vibrated.

Typical measurements of the change of rebound resilience with temperature are shown in Figure 10. These curves have a characteristic shape, all of the curves possessing a well defined minimum which corresponds to a very low value of resilence. At temperatures below the minimum value the resilience increases to a limiting value corresponding to the solid state. The temperature of the minimum depends on the conditions of impact, and for a Lüpke pendulum a minimum value of resilience is recorded at temperatures about 20 to 30 degrees C above the stiffening point. It has been shown that this behavior can be predicted if the time dependence of the high-elastic component of deformation is known.

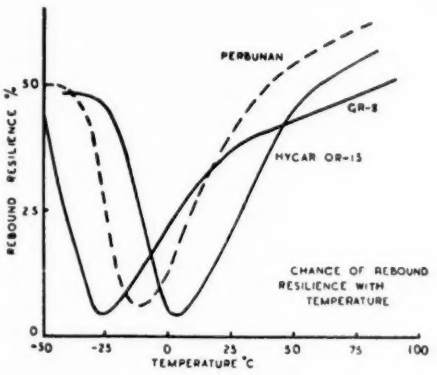


FIG. 10.

At present it is necessary that the relevant test for each specific problem of this type should be performed at low temperatures, but in many cases there will be a relationship with the normal modulus changes. Tener, Kingsbury and Hold[34] have measured the change in tensile strength and elongation at break with decrease in temperature, and have shown an increase in tensile strength and decrease in breaking elongation with the lowering of temperature.

Methods of Cooling.—No mention has yet been made of the effects of either the conditioning and previous history of the sample, or of the methods of cooling the sample. It is well established that both of these items may profoundly influence results, but as yet there is no general agreement as to the experimental procedure to be adopted.

Some rubber vulcanizates exhibit a radical change of properties during prolonged cooling at a constant temperature, and this has been attributed to a change in physical structure resulting from crystallization. There is an optimum temperature at which crystallization takes place most rapidly, the rate of crystallization and the optimum temperature being characteristic of the rubber vulcanizate. Thus the specification of an arbitrary conditioning period and temperature before testing may produce misleading results for certain rubbers.

It is fortunate, however, that most synthetic rubber vulcanizates do not exhibit crystallization, but instead show a transition from an amorphous disorder state to a more ordered state. This transition takes place over a range of temperatures, and Rand, Ferguson and Prather[7] have shown that the ob-

served values of the transition temperatures depend on the rate of cooling, the approach to equilibrium being slower, the lower the temperature. They recommended that for reproducible results the material should be cooled slowly; it appears that at temperatures above the transition temperature, equilibrium conditions are established, and reproducible results can be obtained if the temperature is maintained constant for several minutes. If after longer cooling there is evidence of a lack of reproducibility, then the results indicate that a slow change in structure has taken place (crystallization). The rate at which crystallization takes place is very slow, and experiments which take cognizance of it are time-consuming; furthermore, the progressive stiffening resulting from crystallization is normally incompatible with effective service at low temperatures. Therefore it is considered that stiffness tests should not involve a period of conditioning at low temperatures but should be performed under conditions which are adequate for temperature equilibrium. Data as to whether crystallization is present should be obtained either from repeat tests performed after further cooling or from hardness tests carried out over prolonged periods. Except in the case of Neoprene-GN, none of the synthetic rubber vulcanizates reported in this paper showed any evidence of progressive stiffening during prolonged exposure at low temperatures. The value of the torsion modulus was measured on a variety of synthetic rubbers, which included samples of GR-S, Neoprene-E, Neoprene-GN, Neoprene-I, Neoprene-CG and Thiokol-AZ; the modulus was measured before and during exposure of temperatures of $-10°$ C and $-20°$ C for periods up to 2 hours. The samples of Neoprene-GN, Neoprene-CG, and Thiokol-AZ showed an increase of modulus with the period of exposure; the modulus of the Neoprene-CG vulcanizate was doubled by exposure at $-10°$ C for 1 hour, and at $-20°$ C its modulus was doubled after about two hours' exposure. The increase in modulus of the Neoprene-GN and Thiokol-AZ vulcanizates was much less pronounced, and only a gradual stiffening was experienced during the two hours' exposure.

The two methods of cooling which have been used involve either enclosing the sample in a vessel of cold air or immersing the sample in a cold liquid. The obvious drawback of the first method is that, owing to the low thermal capacity of the air, it takes a relatively long time for the sample to attain the equilibrium temperature. Although rapid cooling of the sample can be produced by a cold liquid, the presence of a cooling liquid may considerably affect the properties of the sample. Rubber vulcanizates swell in most liquids which can be used as cooling agents at low temperatures. This swelling causes both a reduction of the modulus and a reduction of the temperature at which rapid stiffening is evident. Morris, James, Berger and Werkenthin[35] have described the effects of the cooling liquid on the observed values of the brittle points of several rubber vulcanizates. The cooling liquids which they employed were methyl alcohol, isooctane, gasoline and aromatic gasoline. They observed that the effects of the cooling liquid depended on the type of rubber used, and they decided to adopt as their standard value of the brittle point the highest value recorded during experiments done with these four liquids. Although methyl alcohol was the most suitable liquid for Neoprene and Perbunan stocks, isooctane was the best liquid for Hycar OR-15 stocks. Figures 11 and 12 illustrate the different effects which various cooling liquids have on different rubbers; in these experiments the sample was immersed in the liquid for three hours before the commencement of the modulus tests (three hours was somewhat longer than the duration of the modulus test). The Perbunan sample

which had been immersed in acetone showed considerable swelling and consequently a large reduction of both the modulus and the stiffening point, while aviation petrol caused similar effects in a natural rubber sample. Unless there is specific susceptibility of this sort to methyl alcohol it is considered that this last liquid should be used as a cooling agent.

There is, however, yet another complication which may follow from using a cold liquid bath; the liquid besides causing swelling may extract plasticizer from the vulcanizate. Plasticizers normally lower the stiffening point. It is of interest to note that Conant and Liska[22] have reported the possibility of the introduction of a plasticizer causing a raising of the stiffening point. But the replacement of a plasticizer by a solvent more than counterbalances the effect of the loss of the plasticizer, and hence causes a further depression of the stiffening point.

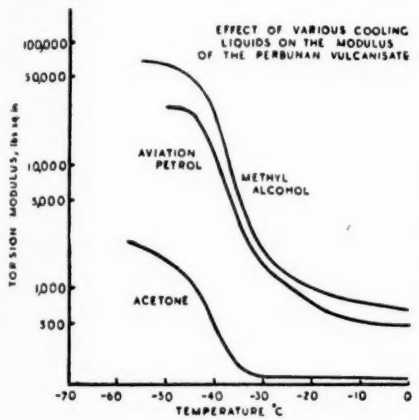


FIG. 11.

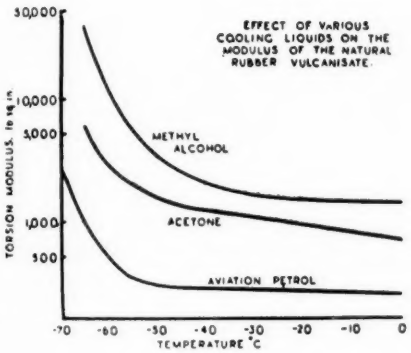


FIG. 12.

ACKNOWLEDGMENT

The author wishes to thank the Research Association of British Rubber Manufacturers for permission to publish this paper.

APPENDIX

COMPOUNDING DETAILS

Ingredient	Natural rubber	Hycar OR-5	Hycar OR-15	Perbunan	Perbunan (A)	GR-S	Plasticised Neoprene GN
Rubber	100	100	100	100	100	100	100
Carbon black	50	50	50	50	50	50	40
Pine tar	4.5	3	—	—	—	3	—
Dibutyl phthalate	—	—	10	10	20	—	—
Light calcined magnesia	—	—	—	—	—	—	4
Stearic acid	2.5	2	0.5	0.5	1	1	2.5
Zinc oxide	5	5	5	5	5	3	1
Mercaptobenzothiazole	0.8	1	—	—	—	1	—
Diphenylguanidine	—	0.2	—	—	—	0.25	—
Dibenzthiazyl disulfide	—	—	1.5	1.5	1	—	—
Tricresyl phosphate	—	—	—	—	—	—	2.5
Sulfur	3	2	1.5	1.5	2	2	2.5

Cured under optimum conditions determined from tensile strength results.

REFERENCES

[1] Graves and Davies, *India Rubber World* **109**, 41 (1943); Liska, *Ind. Eng. Chem.* **36**, 40 (1944).
[2] Alfrey, Goldfinger and Mark, *J. Applied Physics* **14**, 700 (1943); Simha, *J. Phys. Chem.* **47**, 348 (1943).
[3] Kemp, Malm and Winspear, *Ind. Eng. Chem.* **35**, 488 (1943).
[4] Winspear, *Bell Laboratories Record* **22**, 486 (1944).
[5] Bekkedahl and Coworkers, *J. Research Natl. Bur. Standards* **13**, 411 (1934); **15**, 503 (1935); **23**, 571 (1939); **29**, 87, 341 (1942); **33**, 63 (1944).
[6] Davies, Miller and Busse, *J. Am. Chem. Soc.* **63**, 361 (1941).
[7] Rand, Ferguson and Prather, *J. Research Nat. Bur. Standards* **33**, 63 (1944).
[8] Davies, Miller and Busse, *J. Am. Chem. Soc.* **63**, 361 (1941); Alfrey, Goldfinger and Mark, *J. Applied Physics* **14**, 700 (1943); Simha, *J. Phys. Chem.* **47**, 348 (1943); Tuckett, *Trans. Faraday Soc.* **40**, 448 (1944).
[9] Eley, *Trans. Faraday Soc.* **38**, 299 (1942).
[10] Tuckett, *Trans. Faraday Soc.* **38**, 310 (1942).
[11] Church and Daynes, *J. Rubber Research* **4**, 41 (1939).
[12] Yerzley and Fraser, *Ind. Eng. Chem.* **34**, 332 (1942).
[13] Clash and Berg, *Ind. Eng. Chem.* **34**, 1218 (1942).
[14] Imperial Chemical Industries, Ltd., Service Services Rubber Investigations, Users' Memorandum U-7, **1943**, p. 10.
[15] Bilmes, *J. Soc. Chem. Ind.* **63**, 182 (1944).
[16] Koch, *Kautschuk*, **16**, 151 (1940).
[17] Kish, *Rubber Age* (N.Y.) **53**, 131 (1943).
[18] Liska, *Ind. Eng. Chem.* **36**, 40 (1944).
[19] Somerville, *Proc. Rubber Tech. Conf. London*, **1938**, p. 773.
[20] Graves and Davis, *India Rubber World* **109**, 41 (1943).
[21] Morris, James and Evans, *India Rubber World* **110**, 529 (1944).
[22] Conant and Liska, *J. Applied Physics* **15**, 767 (1944).
[23] For example, Kish, *Rubber Age* (N.Y.) **53**, 131 (1943).
[24] Scott, *Trans. Inst. Rubber Ind.* **11**, 224 (1935).
[25] Le Blanc and Kröger, *Kolloid-Z.* **37**, 205 (1925).
[26] Sagajllo, Bobinska and Saganowski, *Proc. Rubber Tech. Conf. London*, **1938**, p. 749.
[27] Morris, James and Evans, *India Rubber World* **110**, 529 (1944).
[28] Church and Daynes, *J. Rubber Research* **5**, 11 (1936).
[29] Gurevich and Kobeko, *Acta Physicochim. U.R.S.S.* **12**, 685 (1940).
[30] Gibbons, Gerke and Tingey, *Ind. Eng. Chem. Anal. Ed.* **5**, 279 (1933).
[31] McCortney and Hendrick, *Ind. Eng. Chem.* **33**, 579 (1941).
[32] Bilmes, *J. Soc. Chem. Ind.* **63**, 182 (1944); Conant and Liska, *J. Applied Physics* **15**, 767 (1944).
[33] Morran, Knapp and Linhorst, *India Rubber World* **100**, 521 (1944).
[34] Tener, Kingsbury and Hold, *J. Research Natl. Bur. Standards* **22**, 367 (1927).
[35] Morris, James and Berger and Werkenthin, *India Rubber World* **108**, 553 (1943).
[36] Aleksandrov and Lazurkin, *Acta Physicochim. U.R.S.S.* **12**, 647 (1940).
[37] Church and Daynes, *J. Rubber Research* **5**, 11 (1936).

HARDNESS TESTS AT LOW TEMPERATURES *

PAUL LAINÉ AND ANDRÉ ROUX

STATION EXPÉRIMENTALE DU FROID DE BELLEVUE, FRANCE

The lack of precision in measuring hardness at low temperatures by the simple method of removing samples from a cold chamber and measuring their hardness as quickly as possible induced the present authors to construct a durometer which is particularly well adapted to studies at low temperatures. This apparatus is shown in its original form in Figure 1.

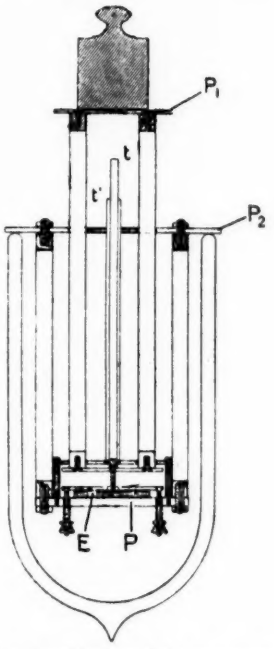


FIG. 1.—Diagram of the apparatus.

The sample, E, is held fast on the bottom support, P, by a steel disc held tight from below by adjustable tension springs. This disc has a hole in its center, through which the penetrating point of the durometer can pass.

The force required for the penetrator to enter the rubber is applied by a weight of 500 grams placed on the platform P_1, and is transmitted to the penetrator by thin maillechort tubes, the heat conductivity of which is low.

* Translated from the *Revue Générale du Caoutchouc*, Vol. 21, No. 9, pages 189–191, September 1944. Reference to this work, which was in progress at the time, was made by Jean Le Bras in a discussion of viscosity, plasticity and elasticity (see *Rev. gén. caoutchouc*, Vol. 20, No. 10, page 200, Oct. 1943). The present paper is a summary of a report made in 1940 in connection with tests which were requested by the Société des Matières Colorantes de Saint-Denis. Since then, similar work has been published by Koch (*Kautschuk* **16**, 151 (1940); RUBBER CHEM. TECH. **14**, 799 (1941)), by Höppler (*Kautschuk* **17**,(1941); RUBBER CHEM. TECH. **15**, 115 (1942)) and by Aengeneyndt and Kesternich (*Kautschuk* **20**, 1 (1944); RUBBER CHEM. TECH. **18**, 401 (1945).

The depth to which the penetrator sinks is estimated by measuring, by means of a spyglass equipped with a micrometer eyepiece, the relative displacement of the concentric maillechort tubes t and t', the first of which is attached to the penetrator and the other to the bottom plate P which supports the sample.

The construction whereby these concentric tubes are attached to their proper fittings is such that there can be no extraneous deformation which might introduce an error into the measurements.

The assembly is supported by plate P_2, which is connected with the base plate P by maillechort tubes. This plate P_2 rests on the open top of a Dewar

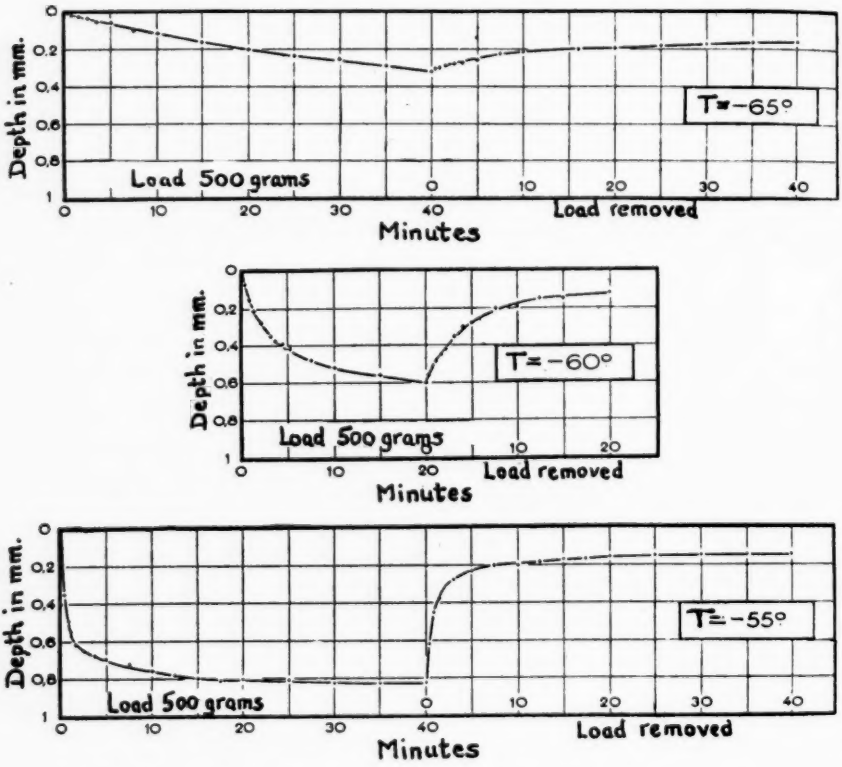


FIG. 2.—Examples of determinations carried out on the same sample, at different temperatures, by the method of chronometric points.

flask, containing acetone, which is cooled by the addition of carbon dioxide snow. Preliminary experiments showed that acetone had no appreciable effect on the particular samples which were being studied. At first the temperature of the acetone bath was measured by an alcohol thermometer, but later resort was had to a resistance thermometer, the sensitive element of which consisted of a coil of fine copper wire resting on the bottom support P. In the first experiments it seemed adequate, as a means of assuring the maintenance of a constant temperature, to add small quantities of carbon dioxide snow periodically to the acetone; later, however, more accurate control of the

temperature was attained by placing around the apparatus, in the acetone, a copper coil, into which was passed, at a velocity controlled by a flowmeter, and by means of a tube with double Dewar walls, air previously chilled in a second coil immersed in liquid air.

The first experiment carried out with this apparatus was with one of a set of samples of rubber which had been found previously to behave particularly well at low temperatures. The temperature of the acetone was approximately −50° C, and the weight applied on the plate was 500 grams. The first striking fact noted was that at this low temperature the point did not penetrate into the rubber instantaneously; in fact even after a quarter hour, the deformation of

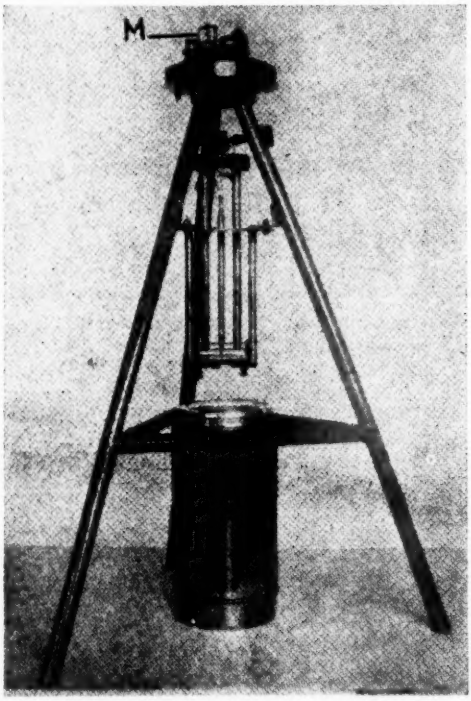


FIG. 3.—The apparatus equipped with a recording device.

the rubber had not reached its maximum value. Equally surprising was the slowness with which the rubber recovered its original form after removal of the load.

These facts were sufficient inducement to trace curves representing as a function of time, the depth to which the penetrator of the durometer sinks while loaded and its rise again after removal of the load. The first three curves which were traced are reproduced in Figure 2. They represent the same sample of rubber at temperatures of −55°, −60° and −65° C. The total time of the experiments at −55° and −65° C was 80 minutes; the total time of the experiment at −60° C was 40 minutes.

These curves show that at low temperatures rubber retains, in spite of its apparent hardness, a considerable part of its elasticity, in addition to which it

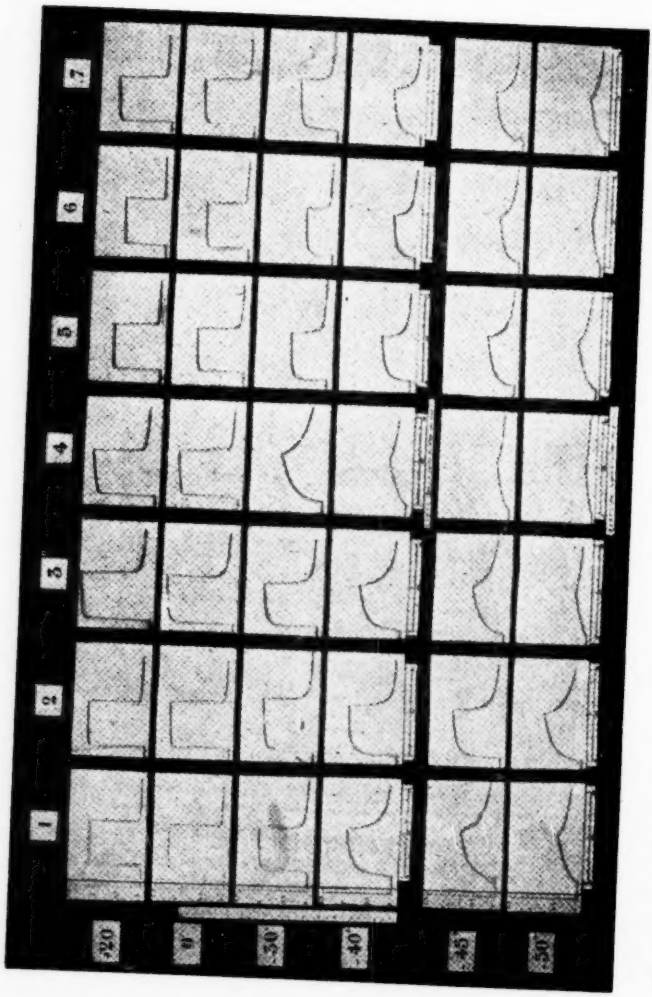


FIG. 4.—Series of recordings of seven different samples at different temperatures. The diagrams in column 3 represent a sample of rubber vulcanized with sulfur alone; those in column 4 represent an Oppanol mixture; those in the other columns represent various rubber mixtures.

exhibits a certain kind of "viscosity", which has a marked curbing action on its deformation. Although the limiting deformations were not reached in the experiments at −60° and −65° C, it appears at first examination that the "viscosity" of rubber is influenced to a much greater degree by a lowering of the temperature than is the deformation under a load, *i.e.*, the coefficient of elasticity. These curves indicate that the potential value of such diagrams in making comparisons of the mechanical properties of rubber products.

In work subsequent to that described in the present paper, it was decided to extend the measurements to somewhat higher temperatures, at which the deformation was too rapid to make it possible to measure it by the method of chronometric points, which had been used up to this time. The apparatus was, therefore, equipped with an automatic registering device. This new form of apparatus, which was constructed in the laboratory with whatever means were available, is shown in Figure 3.

The displacement of the penetrator of the durometer operates the rotation of a mirror through the intermediate action of a system consisting of a wire, a lever, two pulleys and a compression spring. The rotations of the mirror are recorded by means of a photographic registering device.

Figure 4 shows a series of recordings of seven different samples of rubber at temperatures of 20°, 0°, −30°, −40°, −45° and −50° C. The total time of the recordings at 20°, 0°, −30° and −40° was 40 seconds; that of the recordings at −45 and −50° C was 80 seconds. On these last two sets of diagrams the time scale is condensed to one-half the unit magnitude of the other four sets of diagrams.

Although it is hardly possible to deduce from these recordings the true mechanical properties of the rubber samples studied, diagrams of this kind should obviously be of practical interest. By way of example, rubber samples No. 1 and No. 2 had the same composition except for one ingredient in sample No. 2, and also they were vulcanized under the very same conditions. The advantage gained by the addition of the ingredient to sample No. 2 can be clearly seen on the diagrams; this conforms to the fact that among all seven of the samples tested, sample No. 2 was found to behave best at low temperatures.

When it is desired to obtain curves which can be interpreted more easily from a theoretical point of view, it will be necessary to study, not the depth of penetration of the point, but the compression of cylindrical test-specimens or the elongation of threads. The apparatus which has been described can be readily adapted to such measurements.

The apparatus likewise lends itself to tests at elevated temperatures. Such tests have already been carried out, whereby the cold acetone was replaced by glycerol heated by an electrical resistance. The diagrams which have been obtained show that it is possible to follow the increase in plasticity with rise in temperature, and they are of similar interest to those shown in Figure 4.

THE INFLUENCE OF MILLING ON THE PLASTICIZATION OF RUBBER *

ADRIEN HAEHL AND JEAN LE BRAS

INSTITUT FRANÇAIS DU CAOUTCHOUC, PARIS, FRANCE

In the first part of this work[1], the influence of the temperature of the mill rolls and of their friction ratio on the plasticization of rubber was examined in a systematic way. The experiments described in this second paper had as their object the determination of the influence of the speed of the mill rolls, and comprise a series of measurements at three different temperatures, *viz.*, 20°, 60° and 100° C.

The machine and equipment were, as before, a Troester mill, each roll of which was equipped with a temperature control and a speed regulator. In addition a wattmeter made possible the recording of the power consumed by each of the motors.

In general the operating conditions of the previous work, which were described in detail in the previous paper, were followed in the present work.

(1) *Rubber.*—First latex crepe (from the same lot as that used in the first part of the work).

(2) *Mill rolls.*—Diameter 20 cm.; effective length 30 cm.

(3) *Spacing of the mill rolls.*—When loaded, 1 mm.

(4) *Bank of rubber.*—Diameter about 10 mm., which was held constant by decreasing the effective length of the rolls to compensate for successive withdrawing of samples.

(5) *Plasticity measurements.*—Williams apparatus, with test-samples of 1 cc. volume.

The earlier experiments had shown that the use of a differential roll speed is of no advantage in plasticizing rubber; hence all the experiments in the present work were carried out without any friction between the rolls.

The amount of rubber used in each experiment was reduced from 500 grams to 350 grams. It was found that the differential roll-speed reduced the volume of the bank and that the 500-gram units which had been used were a little too much when operating with even speeds, for the bank rolled badly and irregularly. Since the tests were made without friction, it was logical to reduce the size of the load, and after several trials 350 grams appeared to be the most suitable amount. Because of this change in the size of the batch, the plastometric measurements obtained in the present work are not comparable on an absolute basis with those of the first part of the work.

With respect to temperature, it was found that, at a given setting of the temperature-control device, an increase in the speed of the rolls resulted in an

---

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 20, No. 6, pages 111–115, June 1943. The first installment was published in the *Revue Générale du Caoutchouc*, Vol. 19, pages 183–188, July 1942. An abridged version of this first installment was published in *Kautschuk*, Vol. 18, No. 11, pages 144–145, November 1942, and was reprinted (through inability at the time to obtain the complete original paper) in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 17, No. 2, pages 436–440, April 1944.

appreciable elevation in the temperature of the rubber and of the mill rolls. Now it is known that an increase in temperature decreases the effect of mastication; consequently it was essential to take this factor into account. This is the reason why, at predetermined intervals, the temperature of the rubber and that of the back mill roll (whose surface was open to this measurement) were measured by means of a surface pyrometer. In the case of the rubber, this measurement could be made only on a sample which had been removed from the mill, and under these conditions there was a loss of heat between the moment of removal and the actual measurement by the pyrometer. In every case the true temperature of the rubber on the mill was higher than that actually recorded, and all the values should be regarded as minima. It should be pointed out also that the heating of the back roll was higher in the middle than at the ends, where the temperature was practically that of the regulator; hence the temperatures of the middle section which were recorded were maximum temperatures.

As for the roll speeds which were used in the present experiments, these included 12, 18, 24, 30 and 36 turns per minute, which correspond to linear speeds of 7.6, 11.8, 15.2, 19.4 and 22.8 meters per minute.

EXPERIMENTAL RESULTS

The results of the experiments are summarized in Tables 1 and 2 and in Figures 1, 2, 3 and 4. The plasticity values and the elastic recovery values are the mean values of four measurements.

TABLE 1

PLASTICITY AND ELASTIC RECOVERY

Temperature	Roll speed (turns per minute)	Plasticity (height in mm. after mastication for the particular number of minutes)								Elastic recovery (height in 0.01 mm. after mastication for the particular number of minutes)							
		10	20	30	40	50	60	90	120	10	20	30	40	50	60	90	120
20°	12	2.95	2.14	1.85	1.68	1.53	1.46	—	—	27	10	8	7	6	6	—	—
	18	2.49	1.97	1.73	1.59	1.48	1.40	—	—	13	9	7	6	7	6	—	—
	24	2.35	1.87	1.68	1.55	1.44	1.40	—	—	12	8	6	7	7	6	—	—
	30	2.22	1.84	1.65	1.55	1.40	1.40	—	—	10	8	9	9	8	9	—	—
	36	2.12	1.81	1.62	1.55	1.44	1.42	—	—	8	8	8	7	9	8	—	—
60°	12	2.85	2.51	2.25	2.12	2.07	2.01	—	—	21	10	9	8	7	7	—	—
	18	2.65	2.35	2.13	2.07	2.03	2.00	—	—	13	9	7	6	6	6	—	—
	24	2.57	2.27	2.11	2.04	2.03	2.02	—	—	9	7	7	6	7	9	—	—
	30	2.55	2.27	2.09	2.02	2.04	—	—	—	8	7	6	8	7	—	—	—
	36	2.51	2.22	2.07	2.02	—	—	—	—	7	8	8	7	—	—	—	—
100°	12	3.59	3.46	3.28	3.15	3.01	2.89	2.71	2.58	45	34	25	21	19	19	14	12
	18	3.45	3.24	3.08	2.93	2.83	2.72	2.53	—	40	25	17	15	15	14	12	—
	24	3.30	3.05	2.90	2.75	2.63	2.58	—	—	33	21	16	12	11	11	—	—
	30	3.18	2.94	2.75	2.61	2.50	—	—	—	29	18	13	12	12	—	—	—
	36	3.08	2.84	2.67	2.47	—	—	—	—	24	14	10	11	—	—	—	—

To measure the consumption of energy, the power (in kilowatts) absorbed by the motor of each of the mill rolls was measured at predetermined time intervals. The sums of these two values are recorded in Table 2. It should be noted that these values represent the total power consumption, and if it is desired to know the power actually consumed by mastication of the rubber, it is necessary to subtract from these values the power consumed in driving the mill rolls without any rubber on them. This power depends on the speed of the rolls, *e.g.*, it was 1.8 kilowatts for a speed of 12 turns per minute, 2.0 kilo-

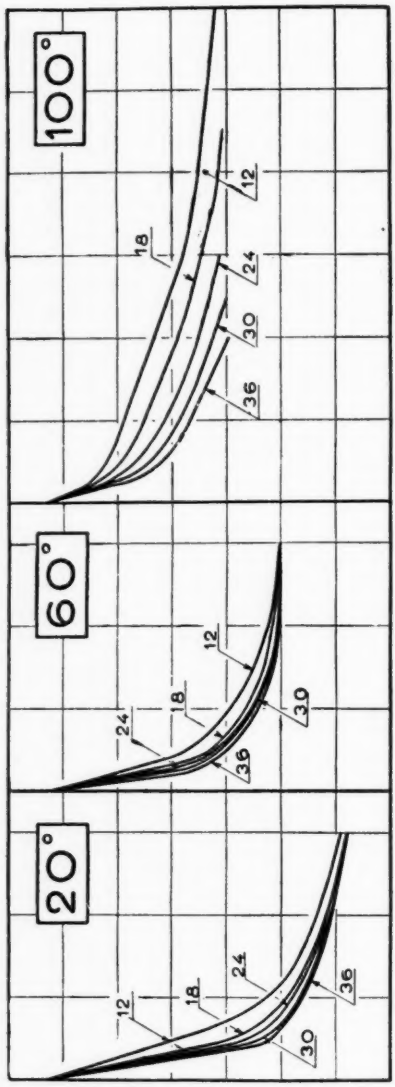


FIG. 1.—Plasticization curves, showing the influence of the speed of the mill rolls and the influence of the temperature.

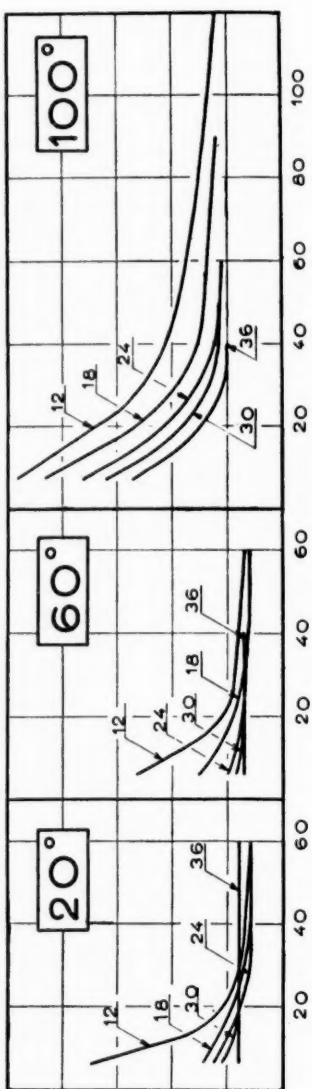


FIG. 2.—Elastic recovery as a function of the time of mastication for different speeds and at different temperatures.

Minutes of mastication

FIG. 2.—Elastic recovery as a function of the time of mastication for different speeds and at different temperatures.

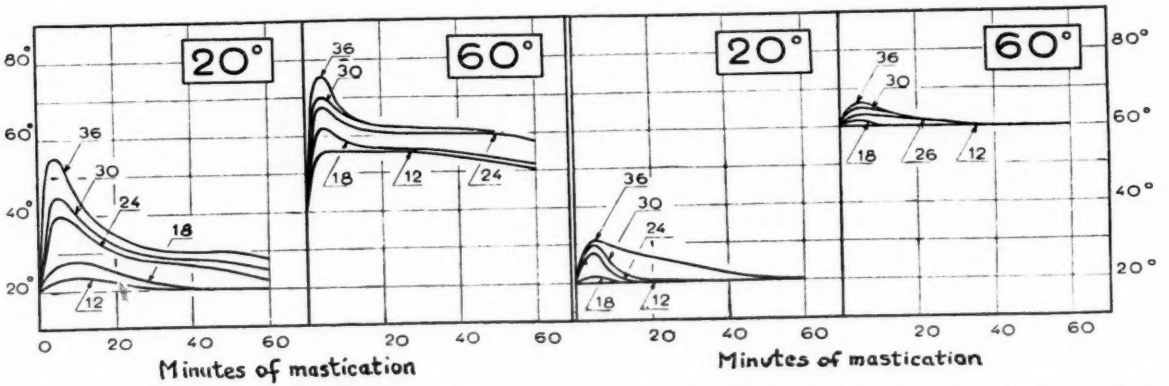


FIG. 3.—Influence of speed of mill rolls on the temperature of the rubber.

FIG. 4.—Influence of the speed of mill rolls on the temperature of the back roll (taken at the middle).

TABLE 2

POWER CONSUMPTION

Temperature	Roll speed (turns per minute)	Power consumed (in kilowatts) by the two motors for the particular number of minutes											
		2	4	6	8	10	20	30	40	50	60	90	120
20°	12	4	4.4	4	3.6	3.4	2.6	2.3	2.3	2.1	2	—	—
	18	4.3	5	4.3	3.8	3.6	2.9	2.7	2.5	2.3	2.2	—	—
	24	5	5.4	5	4.7	4.1	3.6	3.2	3	2.6	2.4	—	—
	30	7.3	6.1	5.2	4.8	4.5	4.1	4.0	3.8	3.6	3.4	—	—
	36	8.6	6.5	5.6	5	5	4.9	4.3	3.9	3.7	3.4	—	—
60°	12	3.5	3.1	3	2.8	2.7	2.5	2.4	2.2	2.1	1.9	—	—
	18	4	3.6	3.4	3	2.8	2.7	2.5	2.3	2.2	2.1	—	—
	24	4.7	4.4	4	3.9	3.7	3.6	3.5	3.3	3.2	3.1	—	—
	30	5.3	4.4	4.2	3.9	3.9	3.7	3.6	3.6	5.5	soft	—	—
	36	5	5	4.7	4.3	4.2	4.1	3.8	3.8	soft	soft	—	—
100°	12	3	2.5	2.4	2.3	2.2	2.2	2.1	2.1	2.1	2.1	2.1	2.0
	18	3.3	2.9	2.7	2.6	2.5	2.5	2.5	2.5	2.4	2.4	2.4	—
	24	4	3.4	3.4	3.4	3.2	3.2	3.1	3.1	3.1	3.0	—	—
	30	4.4	3.8	3.8	3.8	3.8	3.6	3.6	3.4	3.2	soft	—	—
	36	4.8	4	3.8	3.8	3.8	3.4	3.4	3.1	soft	soft	—	—

watts for 18 turns per minute, 2.2 kilowatts for 24 turns per minute, 2.5 kilowatts for 30 turns per minute, and 3.0 kilowatts for 36 turns per minute.

Figure 1 shows the plasticity curves for the various mill-roll speeds which were studied, and for temperatures of 20°, 60° and 100° C. Figure 2 shows the elastic recovery for the same series of experiments.

By way of comparison it may be added that, for the particular crepe rubber used in the experiments, the Williams plasticity before mastication was 4.31 mm., and the elastic recovery was 113 (in 0.01 mm.).

Figures 3 and 4 show the temperatures recorded for the samples of rubber and for the back roll, by the surface pyrometer, under the conditions already described. Heating above the theoretical temperature of the experiment was particularly important at the beginning of mastication, and above all in experiments at 20° C, where, with a roll speed of 36 turns per minute, the temperature approached 60° C. Later the temperature tended to become stabilized at the point set by the temperature controller. It will be noted that at 60° C the recorded temperatures are in some cases lower than the theoretical values. This is explainable, as has been pointed out above, by the unavoidable losses of heat during the measurements, and means that the true temperatures must have been higher by perhaps ten degrees than the recorded temperatures. In the tests at 100° C, these heat losses were so great that the curves which were recorded have no real significance. However, since the temperature of the back roll remained at all times at practically 100° C, it is safe to assume that even in this case there was no appreciable additional heating of the rubber.

Influence of the speed of the mill rolls on the plasticity.

The curves in Figure 1 show that the speed of the rolls has an important influence on the plasticization of rubber. This is particularly evident when, as has been done in Figure 5, the time of milling necessary to reach a Williams plasticity of 2.5 is plotted as a function of the speed of the mill rolls. It should be pointed out that the curves for temperatures of 20° C and 60° C would be much less flat if the heating of the rubber above the theoretical temperatures

of the experiments did not happen to counteract the effect of milling. If this were not so, the groups of curves for 20° and 60° C would not be so closely bunched together.

In considering this influence of the speed of the mill rolls, it could well be asked whether the plasticity is not merely proportional to the number of times that the rubber passes between the mill rolls, *i.e.*, the speed of the rolls. This is not, however, actually the case, probably because of heating of the rubber and also because of the dragging action which the rubber undergoes, which increases with increase in the speed of the rolls, and which must influence its milling within the bank of rubber.

To show this more clearly, the times of milling necessary to reach a series of Williams plasticities shown in the upper line of Table 3 were obtained from the curves in Figure 1. These times were converted to the theoretical times at

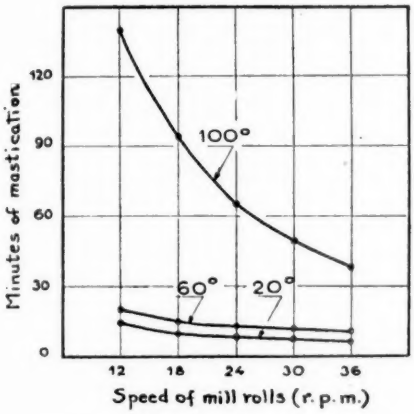


FIG. 5.—Curves showing, as a function of the speed of the mill rolls and for different temperatures, the times of mastication necessary to reach the Williams plasticity of 2.5.

which these plasticity values should be obtained if the product of the roll speed by the time of milling were constant, taking as a basis the product of the lowest speed used (12 turns per minute) and the corresponding time of milling. The results are shown in Table 3, from which the following facts are evident.

TABLE 3

	Williams plasticity	3.1	3	2.8	2.6	2.5	2.4	2.3	2.2	2.1	2	1.75	1.50
	12 turns	—	—	—	1	1	1	1	1	1	1	1	1
	18	—	—	—	1.00	1.03	1.07	1.15	1.18	1.21	1.19	1.25	1.33
20°	24	—	—	—	1.10	1.10	1.19	1.29	1.37	1.20	1.32	1.49	1.67
	30	—	—	—	1.20	1.21	1.25	1.32	1.38	1.49	1.56	1.71	2.08
	36	—	—	—	1.22	1.25	1.23	1.34	1.35	1.50	1.63	1.88	2.50
	12	—	—	—	1	1	1	1	1	1	—	—	—
	18	—	—	—	1.01	1.10	1.18	1.20	1.19	1.17	—	—	—
60°	24	—	—	—	1.18	1.21	1.31	1.38	1.37	1.37	—	—	—
	30	—	—	—	1.32	1.40	1.54	1.64	1.64	1.66	—	—	—
	36	—	—	—	1.40	1.54	1.73	1.84	1.88	1.92	—	—	—
	12	1	1	1	1	1	—	—	—	—	—	—	—
	18	1	1.05	1.14	1	1.01	—	—	—	—	—	—	—
100°	24	0.86	0.94	1.07	0.94	0.93	—	—	—	—	—	—	—
	30	0.81	0.90	1.04	0.87	0.89	—	—	—	—	—	—	—
	36	0.63	0.78	1.02	0.87	0.81	—	—	—	—	—	—	—

(1) At 20° and at 60° C the quotients are close to 1, *i.e.*, the time of milling is proportional to the speed, provided low speeds are used and plasticization is not carried too far. With higher speeds, and particularly if milling is continued until the rubber has become very plastic, the times of milling become progressively higher than the times calculated by the proportionality formula.

(2) At 100° C proportionality is approached fairly closely; however, at high speeds, the quotients are, contrary to those at 20° C and 60° C, considerably below 1. This indicates that the times of milling are shorter than called for by theory; *e.g.*, for a plasticity value of 3.1 and speed of 36, the time of milling found experimentally is 37 per cent lower than the calculated time.

These various facts show that, to obtain any desired plasticity, there is little to be gained from the point of view of time, by increasing the speed when operating at temperatures of 20° and 60° C. On the contrary, when operating at 100° C, the gain in time increases almost proportionally to the speed.

It is probable that this would be equally true at 20° and 60° C if the temperature of the rubber could be maintained at exactly the point desired. But these are only theoretical considerations, and it is necessary to conform to experimental conditions which can be realized in practical milling operations.

Influence of the speed of rolls on elastic recovery.

The phenomena are as well defined as in the plasticity measurements, and lead to similar conclusions.

An examination of Figure 2, for example, makes it evident that, at temperatures of 20° and 60° C, the increase in mill-roll speed decreases the elastic recovery appreciably only during the earliest stage of the milling process; after about twenty minutes, the elastic recovery tends toward a lower limit which is practically independent of the speed of the mill rolls. It will be noted also that, at high speeds, this limit becomes slightly higher than the limits at slower speeds. This inversion must unquestionably be attributed to the considerable heating of the rubber, the effect of which is the opposite of that of mastication.

At 100° C the decrease in elastic recovery is proportional to the speed of the rolls.

Consequently the use of high speeds is of advantage only at relatively high operating temperatures, or in cases where only relatively little plasticization is desired and the elastic recovery at the same time is to be as low as possible.

Influence of the speed of the mill rolls on the power consumption.

The experimental data in Table 2 can be utilized to construct curves showing the power absorbed by the two motors as a function of the time of milling. If then the times of milling t required to reach the Williams plasticity value of 2.5 at the different temperatures and different roll speeds are considered, the total power required to attain this plasticity is obtained by estimating the surfaces bounded by the curves mentioned between the origin of the coördinates and these t abscissas. These calculations give the results summarized in Table 4, and include the total power consumed and, by deduction of the power consumed by the motor itself, the power consumed by the work of plasticization itself.

In this way it was proved that the total operating power required to obtain a given plasticity remained practically constant at 20° C and 60° C, irrespective of the speed of the mill rolls. At 100° C, on the contrary, the power consumption decreased considerably as the roll speed increased, *e.g.*, it became

TABLE 4

POWER CONSUMED TO REACH A PLASTICITY OF 2.5

Temperature	Speed of rolls (r.p.m.)	Time of milling (min.)	Power consumption	
			Total	Rubber alone
20°	12 turns	14.5	0.89	0.46
	18	10	0.72	0.38
	24	8	0.67	0.38
	30	7	0.75	0.45
	36	6	0.75	0.46
60°	12	20.5	0.97	0.38
	18	15	0.82	0.32
	24	12.5	0.85	0.40
	30	11.5	0.85	0.37
	36	10.5	1.00	0.42
100°	14	140	5.00	0.81
	18	94	3.92	0.80
	24	65.5	3.66	1.10
	30	50	2.93	0.96
	36	38	2.33	0.43

twice as great when the speed was decreased from 36 to 12 turns per minute. A comparison of Figures 5 and 6 shows a striking similarity in character, and both illustrate the decided change in the nature of the phenomena when the temperature was increased well above 60° C. As has already been pointed out more than once in the first part of this work, the temperature of 60° C appears to be a critical temperature in plasticizing rubber.

It is evidently the total power consumed which must be taken into account from a practical point of view. Nevertheless it is interesting to note that, as far as the power consumed for plasticizing alone is concerned, even at 100° C it changed relatively little with change in the roll speed, at least up to 30 turns per minute. Above this latter speed, the power consumed for plasticizing decreased greatly and at 36 turns per minute it was practically the same as at 20° and 60° C.

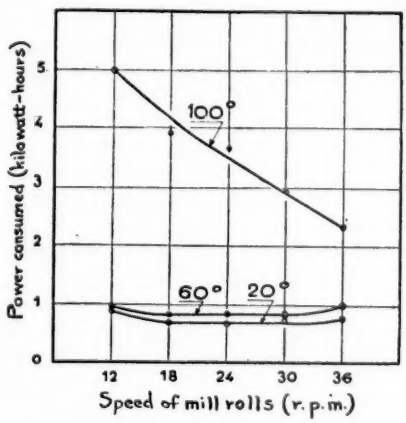


FIG. 6.—Curves showing, as a function of the speed of the mill rolls and for different temperatures, the electric power consumed to reach the Williams plasticity of 2.5.

COMPARISON WITH THE SURFACE ASPECT

As in the earlier work, observations were made of the apparent indications of plasticization which in many factories still serve for judging the time and degree of plasticization. In comparing these observations with the true plasticity values measured by the Williams apparatus, a new opportunity was had to prove to what extent these phenomena may lead to erroneous conclusions.

When the disappearance of holes, the smoothness of the surface, or the transparency of the sheet from the mill rolls is used as a basis for judging plasticization, the indications are more often than not at variance with the results obtained by the plastometer. If, for example, a record is kept for each test of the time required for the holes in the sheet to disappear, results such as those shown in Table 5 are obtained.

TABLE 5

DISAPPEARANCE OF HOLES (APPARENT PLASTICIZATION)

Speed of mill rolls (turns per min.)	20° C		60° C		100° C	
	Minutes of milling	Williams plasticity	Minutes of milling	Williams plasticity	Minutes of milling	Williams plasticity
12	55	1.48	15	2.65	5	3.80 (approx.)
18	19	2	10	2.65	2.30	4 (approx.)
24	15	2.08	7	2.65 (approx.)	2	4.05 (approx.)
30	12	2.12	4	2.85 (approx.)	1.45	4.10 (approx.)
36	8	2.23	2	3.20 (approx.)	1.20	4.15 (approx.)

A comparison of the number of minutes of milling for all holes to disappear with the Williams plasticity at the time (values obtained from the curves in Figure 1 for the corresponding times) makes it evident that there is no correlation between the disappearance of holes in the sheeted rubber and its true plasticity. Thus at 100° C and a speed of 36 turns per minute, the Williams plasticity was 4.15 when the holes disappeared, whereas at 20° C and at 20 turns per minute it was only 1.48 when they disappeared.

PRACTICAL CONCLUSIONS

A survey of the results obtained by a systematic study of the influence of the speed of the mill rolls on the plasticization of rubber, as measured by the compression of a sample in the Williams plastometer, leads to certain definite conclusions.

(1) To obtain a predetermined degree of plasticity in a minimum length of time, a real advantage can be gained by increasing the speed of the mill rolls only if the milling operation is carried out at relatively high temperatures, *i.e.*, above 60° C. At 100° C the saving in time by increasing the speed is almost proportional to the speed of the rolls.

(2) There is an analogous effect with respect to the power consumption. At 20° and 60° C the power consumed is practically independent of the speed of the mill rolls, but at 100° C it decreases rapidly with increase in the speed of the rolls.

Certain conclusions of direct practical value also may be drawn from the work.

When operating at 20° or at 60° C, an increase in the speed of the rolls has a slightly favorable effect in that the time of milling required to reach a given plasticity can thereby be slightly reduced. At 100° C, the saving in time is much greater and is accompanied by an equally important saving in power consumed.

In brief, under conditions still so common in practice, where rubber is plasticized on a roll mill, the speed of rotation of the mill rolls is a factor of no great importance.

REFERENCE

[1] Haehl and Le Bras, *Rev. gén. caoutchouc* **19**, 183 (1942); RUBBER CHEM. TECH. **17**, 436 (1944).

THE ACCELERATED VULCANIZATION OF EBONITE*

B. L. DAVIES

DEPARTMENT OF CHEMISTRY AND RUBBER TECHNOLOGY,
NORTHERN POLYTECHNIC, LONDON, ENGLAND

INTRODUCTION

The essential property of ebonite is its rigidity at ordinary temperatures, and the purpose of vulcanization is to bring it to this state. Accordingly hardness measurements represent a valuable and at the same time simple and rapid method for controlling vulcanization. The Shore durometer is a very useful instrument for studying soft vulcanized rubber, but it does not serve to distinguish between very hard rubber products. Nevertheless, by measuring the hardness of ebonite at different degrees of vulcanization and plotting these values as a function of the time of heating, curves of great significance are obtained, as is shown in the three figures in the present paper.

Each curve consists of two parts, the second of which is formed of a straight line representing the reaction, properly speaking, which leads to the formation of ebonite. When prolonged upwards, this straight line cuts the ordinate corresponding to a hardness of 100 per cent at a point which indicates the time of heating required to attain complete hardness. It has already been shown[1] that the best mechanical properties are obtained at this particular state of vulcanization.

When it is desired to study the acceleration of an ebonite mixture, it is advisable to prolong the straight line downwards to the point where it cuts the hardness axis so as to determine this position and the slope A knowledge of this slope, which is represented by the symbol r, makes it possible to measure the rate at which ebonite is formed, and every change in location where this straight line cuts the hardness axis (the ordinate value being represented by f) corresponds to a displacement of the entire curve.

The equation of this straight line is, then:

$$H = rt + f$$

where H is the hardness (in percentage) and t is the time of heating in minutes.

FACTORS WHICH INFLUENCE THE SLOPE

It has already been proved[2] that every change in composition of a mixture or in the conditions of heating which tends to change the rate of chemical combination of sulfur results in a corresponding change in the slope of the straight line. For example, an elevation in temperature or an increase in the sulfur content or accelerator content increases the slope of the curve without, however, displacing it otherwise.

A few examples may be cited to confirm this fact. In the case of a mixture containing rubber 100, sulfur 50, zinc oxide 5 and stearic acid 0.5, the slope of

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 18, No. 8, pages 268–271, October 1941. This paper was presented at the Rubber Congress in Paris, May 1940.

the straight line increased from 0.30 for vulcanization at 140° C to a value of 0.76 for vulcanization at 150° C and to a value of 2.15 for vulcanization at 160° C. Based on these values, the temperature coefficient of vulcanization of ebonite is approximately 2.65.

Influence of accelerators.

When mercaptobenzothiazole was added to the foregoing ebonite mixture and the mixture was vulcanized at 150° C, the following values of the slope r were obtained.

Accelerator (percentage of rubber)	0.5	0.75	1.0	1.5	3	7.5	10
Value of r	0.73	0.82	0.93	1.06	1.40	1.92	1.92

It was found that an increase in accelerator content gave a corresponding increase in the value of r, which reached a maximum value, R, without any resultant displacement of the curves. All the curves with the exception of the last started at the same point of origin. When, at the point at which the maximum value R was attained, more accelerator was added, the slope remained the same but the entire curve was displaced upwards; in other words, there was an increase in the value of f.

Similar results were obtained with other accelerators, and it is of interest that the maximum R values of the slopes found for nine different accelerators were almost the same, but that the percentages of the accelerators required to obtain the maximum slope were widely different. This indicates that different accelerators are not effective to the same degree. It is interesting to examine this order of effectiveness, for it is a rather surprising one, as the examples in Table 1 will show.

TABLE 1

Accelerator	Percentage	Maximum slope
Mercaptobenzothiazole	7.5	1.92
A-19	3.0	2.04
Vulcafor-RN	2.5	1.81
Diphenylguanidine	1.5	1.86
Di-*o*-tolylguanidine	1.5	1.85
Vulcacit-CT	1.5	2.03
Zinc diethyldithiocarbamate	1.5	2.00
Tetraethylthiuram disulfide	0.7	2.10
Zinc pentamethylenedithiocarbamate	0.7	1.77

In further experiments, results only very little different from those above were obtained. The basic accelerator, diphenylguanidine, when used in conjunction with mercaptobenzothiazole, is known to give the effect of double acceleration in the vulcanization of soft rubber, particularly when these two accelerators are used in equal proportions[3]. The data in Table 2 show that it is likewise possible to increase the efficiency of acceleration in vulcanizing ebonite by the use of these two accelerators conjointly.

TABLE 2

Diphenylguanidine (percentage)	r	Mercaptobenzothiazole (percentage)	r	Diphenylguanidine mercaptobenzothiazole (percentage)	r
0.5	0.9	4	1.22	0.5	0.97
1.0	1.17	6	1.64	1.0	1.32
1.15	1.54	7	1.84	1.5	1.77
2.0	1.70	8	1.84	2.0	1.78
2.5	1.71	—	—	—	—

Similar results were obtained with mixtures of diphenylguanidine and tetraethylthiuram disulfide. However, with such combinations of accelerators, the maximum rate of hardening is not increased, and the only advantage is a reduction in cost resulting from the greater efficiency of the combined accelerators.

If the curves which have just been described for the unloaded mixtures are prolonged downwards, they all pass approximately through the origin of the coördinates; in other words, the value of f is zero. Likewise the mean value of the maximum slope R for all these accelerators is 1.9. The expression $H = Rt + f$, can therefore be used to calculate the time of vulcanization at 150° C of an unloaded mixture containing one of the foregoing accelerators in the desired percentage to obtain the maximum acceleration. However, since it is the hardness of 100 per cent which is desired, the equation can be simplified to:

$$100 = 1.9\,t$$

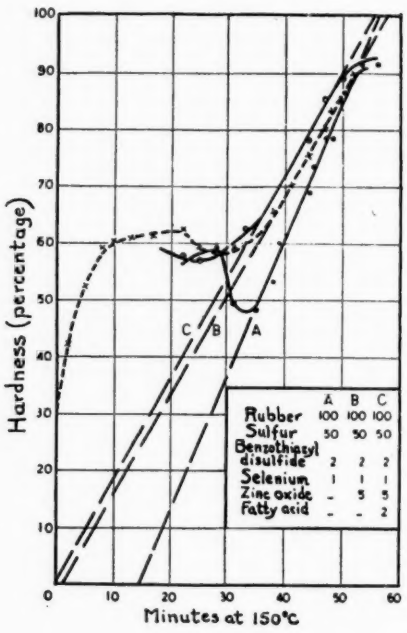


FIG. 1.

Influence of the type of crude rubber.

It is well known that the time of vulcanization required to reach the normal state of soft vulcanized rubber varies from lot to lot of crude rubber, depending on the source of the rubber. It seemed, therefore, of interest to study the influence of this variable on the formation of ebonite. To this end sulfur was added to different samples of rubber in the proportion of 50 parts to 100 parts, and the mixtures were vulcanized, without the addition of any accelerator, in a press at 150° C. Other mixtures were accelerated, by adding 0.5 part of diphenylguanidine, 0.5 part of tetramethylthiuram disulfide and 5 parts of zinc oxide per 100 parts of rubber. The results are given in Table 3.

TABLE 3

Rubber	Unaccelerated r	Accelerated R
Air-dried sheet	0.39	1.85
Pale crepe	0.37	—
Brown crepe	0.50	1.65
Smoked sheet	0.37	—
Pale crepe	0.39	1.82
Smoked sheet	0.50	1.77
Hard fine para	0.41	1.80

The data in Table 3 show that the variability which crude rubber manifests when no accelerator is employed disappears almost entirely when the rubber is accelerated. This variability is probably related in some way to the presence of certain natural accelerators in crude rubber. Analyses have shown that the rate of vulcanization is not directly proportional either to the total nitrogen content or to the acidity.

FACTORS LEADING TO DISPLACEMENT OF THE CURVE

In the experiments just described, it will be seen that, except in cases where the mixture contains a percentage of accelerator in excess of that necessary to obtain the maximum acceleration, all the curves start from the origin or from a point close to the origin of the coördinates. The observation suggested the possibility that the excess of accelerator acts as a filler, and was an inducement to study mixtures containing an inorganic filler so as to determine in what way such a loading displaces the curve. To this end, the values of f for different percentages of several commonly used fillers were determined.

TABLE 4

f VALUE WITH DIFFERENT FILLERS

	Clay			Magnesium carbonate			Talc			Bitumen		
Percentage (by volume)	10	20	40	10	20	40	10	20	40	12.5	25	50
f Value	13	19	29	38	50	71	8	20	30	6.5	11	13

The data in Table 4 bring up the question of the influence of the zinc oxide used in the accelerated mixtures already studied. To answer this question a new mixture was prepared, to part of which accelerator alone, to another part of which accelerator and zinc oxide, and to a third part of which accelerator and zinc oxide and fatty acid, were added. The curves in the three diagrams show the results obtained.

The influence of zinc oxide in mixtures containing accelerators.—The addition of a fatty acid to a mixture containing an accelerator and an activator does not bring about any change in the rate of hardening, but does bring about a slight displacement of the curve, downwards in the case of diphenylguanidine, and upwards in the case of acidic accelerators. This displacement downwards indicates that the fatty acid has a softening effect, the nature of which is probably analogous to that of fillers, but in the opposite sense. Such an action was foreseen, and it indicates that the slight displacement upwards in the other cases is of real significance. It is, of course, generally assumed that a state of acidity is an essential condition for mercaptobenzothiazole and benzothiazyl disulfide to function satisfactorily as accelerators of vulcanization of soft rubber.

The curves of the mixtures which did not contain any activator have, in all cases, relatively steep slopes and also are displaced downwards. All the curves cut the hardness axis at points which are considerably below the origin of the coördinates. This is not in general the case with simple mixtures of rubber and sulfur which contain no accelerators. It appears, therefore, that the phenomenon of initial softening is a specific effect of accelerators.

It is difficult to place any significance on a negative hardening, and it is more reasonable to start the curves at points on the time axis. This would indicate that the beginning of the reaction which leads to the formation of ebonite is retarded when the mixture contains an accelerator but is not activated. The fact that there is no such retardation in a great number of unaccelerated mixtures shows that the retardation cannot be attributed to insufficient thermal conductivity, but rather to a specific effect of the accelerator.

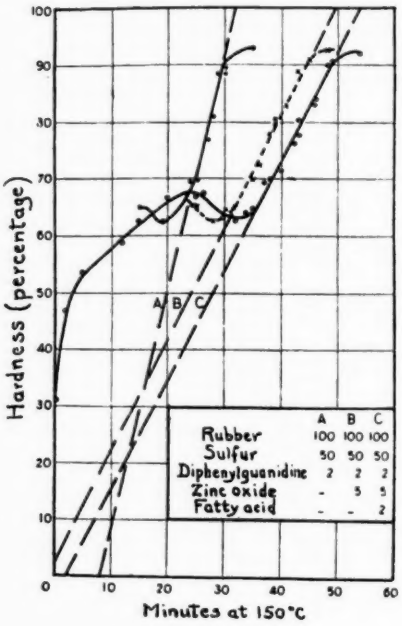


FIG. 2.

It is remarkable to find that, in those mixtures which contained an acid accelerator which was not activated, the total times of vulcanization were the same as those of the corresponding activated mixtures. The relatively steep slopes of the curves compensate for the initial retarding effects. In the case of the mixtures containing diphenylguanidine, the slope of the unactivated mixture is so steep in relation to the small retarding effect that the unactivated mixture reached a hardness of 100 per cent in a shorter time than did the mixture containing the activator.

Influence of the rubber and degree of mastication.—An examination of curves of unaccelerated mixtures which were prepared with different types of crude rubber show that they do not all start at the origin of the coördinates. It was

thought at first that this divergence was purely accidental, but a more thorough investigation showed that it may be of real significance.

Although the conditions of vulcanization were automatically controlled, it is possible that there were accidental variations during the vulcanizing operation, which were responsible for the displacement of some of the curves, by, for example, causing an initial retardation in the heating of the samples. It is necessary, therefore, in comparing values of f, to operate under identical conditions so as to obtain values which represent samples vulcanized for the same length of time. This is what was done with the sets of samples which are grouped together in Table 5. It is evident, then, that samples with the lowest r values had the highest f values, and conversely.

TABLE 5

Rubber	r	f
Smoked sheet	0.37	+6
Air-dried sheet	0.39	+8
Brown crepe	0.50	+3
Pale crepe	0.37	+1
Pale crepe	0.39	−6
Smoked sheet	0.50	−16
Rubber (not identified)	0.57	−21

Since there is apparently no relation between the r and f values and the content of nonrubber components naturally present in different rubbers, it must be concluded that the physical state of the rubber is responsible for these differences.

To verify this point, mixtures were prepared from a sample of rubber which had been milled for various lengths of time at 50° C, and to which sulfur was then added. Vulcanization curves of these mixtures were obtained, and from them the r and f values shown in Table 6 were derived.

TABLE 6

Time of mastication (minutes)	r	f
15	0.57	−21
25	0.65	−30
35	0.70	−40
55	0.61	−49

The data in Table 6 show that, with continued mastication of the rubber before mixing, the curves are displaced downwards, and that this displacement is accompanied by an increase in the rate of hardening. If these conclusions are compared with those arrived at from an examination of the accelerated and unactivated mixtures described above, it will be evident that the accelerator itself brings about physical and physico-chemical changes which are strictly analogous to those resulting from prolonged mastication.

It is equally interesting to note that, in this last series of experiments, as in the preceding ones, the four curves meet at approximately the same point on the ordinate, corresponding to a hardness of 100 per cent.

RÉSUMÉ AND CONCLUSIONS

The curve of the changes in the hardness of a rubber mixture with high sulfur content as a function of the time of vulcanization is composed of two

parts, the second of which is a straight line. The slope of this second part represents a valuable measure of the rate of hardening. If this rectilinear part of the curve is prolonged downwards, it passes in many cases through the origin of the coördinates. Since the time of vulcanization required to reach a hardness of 100 per cent is determined by the slope of the rectilinear part of the curve and by the position of its origin, the factors which have an influence on these two characteristics were studied.

The rectilinear part of the curve can be represented by the equation: $H = rt + f$, where H is the hardness (expressed in Shore units), r is the rate of hardening or the slope of the line (expressed in percentage hardness per minute), t is the time of heating in minutes, and f is the ordinate of the point where the straight line cuts the hardness axis. This equation can be used to calculate the time required to vulcanize mixtures to the ebonite state.

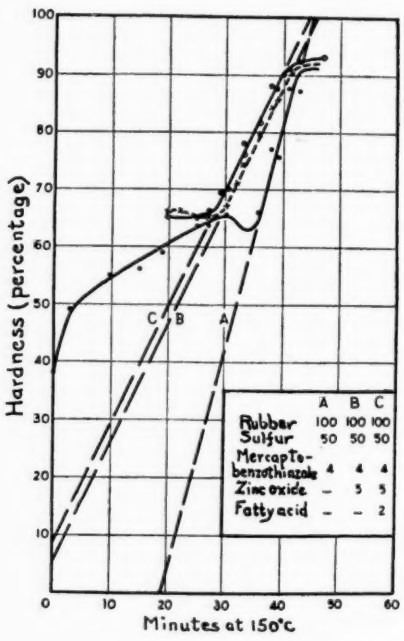


FIG. 3.

The value of r is affected by the temperature of vulcanization (it increases about 2.65 times for each increase in temperature of 10° C) and by the percentage of accelerator in the mixture. An increase in accelerator content increases the rate of hardening at 150° C, and this rate reaches a maximum of approximately 1.9 with most accelerators. The order of efficiency of accelerators varies considerably and it is not the same for ebonite as it is for soft rubber, as has been shown by several examples. It is possible to increase the efficiency of accelerators by the use of secondary accelerators. The values of r are greater when the accelerated mixtures do not contain zinc oxide.

The value of f is practically equal to zero, for unloaded mixtures, the rubber of which has been normally masticated, and which contain an accelerator and

zinc oxide as activator. The value of f is increased by the addition of fillers to an extent which depends on their nature and the proportion added. Data have been presented to show the effects with different percentages of some common fillers. Light magnesium carbonate had the greatest effect. When present in excess, accelerators behave as fillers. If a mixture contains no zinc oxide, f decreases more in the case of mixtures containing acid accelerators than it does in the case of mixtures containing diphenylguanidine. Stearic acid lowers slightly the value of f, particularly in mixtures containing diphenylguanidine. Excessive mastication likewise decreases the value of f.

There are various conditions necessary to obtain rapid vulcanization at any given temperature.

First it is necessary to use the percentage of accelerator which gives the true maximum acceleration. In this case the choice of the type of accelerator becomes simply a question of cost.

Since zinc oxide causes hardening to start rapidly, it is advantageous to use this material in mixtures which are accelerated by mercaptobenzothiazole and benzothiazyl disulfide, and which are to be molded. The total time of vulcanization is, however, not reduced by the addition of zinc oxide. The use of zinc oxide in mixtures containing diphenylguanidine should be avoided, except perhaps for thick objects, for it increases the total time of vulcanization.

Too long mastication should be avoided, for it retards the onset of hardening; it does not, however, increase the total time of heating.

With ordinary types of rubber, the addition of a fatty acid is not necessary. It is of no advantage in mixtures containing mercaptobenzothiazole or benzothiazyl disulfide, and it retards the onset of hardening of mixtures containing diphenylguanidine.

In using light magnesium carbonate as filler, the maximum percentage compatible with the particular type of mixture can be used satisfactorily.

The variability of crude rubber is of relatively little importance in the vulcanization of ebonite, for the lack of uniformity disappears when an accelerator is added to the mixture. On the contrary, with mixtures containing no accelerator, different rubbers show differences which are manifest in the rate of hardening and to a lesser extent in the time required for hardening to begin. These differences may be attributed to differences in physico-chemical state, resulting, at least in part, from the effects of natural accelerators in the rubbers. Accelerators which are not activated bring about changes of greater magnitude, but the nature of which appears to be similar.

REFERENCES

[1] Davies, *Trans. Inst. Ruber Ind.* **9**, 130 (1933).
[2] Davies, *Trans. Inst. Rubber Ind.* **10**, 176 (1934); RUBBER CHEM. TECH. **8**, 175 (1935).
[3] Jones, *Trans. Inst. Rubber Ind.* **9**, 332 (1934).

A STUDY OF THE RUBBER-METAL BOND *

S. Buchan and J. R. Shanks

Although the practice of bonding rubber to metal has been in use for many years, no theories appear to have been advanced which explain adequately the mechanism of bonding. It has been stated that the brass bond between rubber and metal functions through chemical linkages, but this can only be regarded as tentative and has yet to be proved. No attempt has been made to find out how ebonite functions as a bonding medium or the more recently discovered derivatives of rubber, such as sulfonated rubber, chlorinated rubber, and rubber hydrohalides. Until it is properly elucidated just how bonding agents do act, further logical development of improved bonding media cannot be pursued. It is intended in this paper to show how the rubber-metal bond behaves at subnormal temperatures and how a low temperature technique may be used for studying the mechanism of bonding.

The effect of low temperatures on the tensile strength and associated properties of vulcanized rubber, such as hardness, permanent set, flexibility, resilience and flexing, has been dealt with fairly comprehensively in the literature. Progressive reduction in temperature leads to only a moderate increase, for example, in tensile strength, until the point is reached at which the rubber stiffens and freezes, when a marked increase occurs. Examination of a brass-bonded unit at low temperatures revealed that the graph obtained for bond strength was very similar in slope and character to that for tensile strength. The similarity is illustrated by the data in Table 1 and in Figure 1.

Table I

Effect of Low Temperatures on Bond Strength

Temp. (°C)	21.1	0	−20	−30	−40	−50	−55	−60
Bond strength (lb. per sq. in.)	813	915	1091	1116	1243	1817	2506	2770

The actual relationship, if any, between rubber strength and bond strength at normal and subnormal temperatures, however, needed further investigation to see whether the one was dependent on the other. Previous experiments appeared to indicate that the bond strength was independent of rubber strength. Briefly, the facts supporting this belief at this stage were as follows. First a nonreinforced compound consisting of 100 parts rubber and 5 parts sulfur, with a tensile strength of 220 lb. per sq. in., gave a corresponding bond strength at room temperature of 330 lb. per sq. in. and at −55° of 2190 lb. per sq. in.; whereas a reinforced and accelerated compound with a tensile strength at room temperature of 3300 lb. per sq. in. and a corresponding bond strength of 813 lb. per sq. in. gave a breaking load of 2500 lb. per sq. in. at −55° C. Secondly, a nonreinforced compound consisting of 100 parts rubber, 5 parts sulfur and 2 parts selenium gave a tensile strength of 626 lb. per sq. in. and a bond break at −55° C of 2800 lb. per sq. in., which was higher than that recorded by the strongly reinforced quality mentioned. These two results seemed to

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 21, No. 4, pages 266–278, December 1945.

indicate that bond strength was independent of rubber strength; otherwise it is difficult to explain why rubbers, weak at normal temperatures, should give bond strengths at low temperatures as high or even higher than those obtained with much stronger and tougher rubbers.

To confirm that bond strength was not dependent on rubber strength, a series of experiments were initiated. Five rubber stocks (JA–JE) were compounded to give a series of mixtures with graded tensile properties. They were prepared so that the ingredients which were altered to give the variation in physical properties would not appreciably affect the bonding capabilities of the mixings. In other words, the effect on the bond strengths, due to causes other than the lowering of the temperature, would be caused by differences in the physical strength of the rubbers and not by any change in chemical action at the bonding interface.

	JA	JB	JC	JD	JE
Rubber	100	100	100	100	100
Whiting	—	25	50	100	200
Soft black	50	25	—	—	—
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Pine tar	2	2	2	2	2
Sulfur	3	3	3	3	3
Phenyl-β-naphthylamine	1	1	1	1	1
Accelerator	1	1	1	1	1
	164	164	164	214	314
Tensile strength (lb. per sq. in.)	3640	2970	2690	2090	1000
Elongation at break (percentage)	612	625	675	600	416

The effect of a range of temperatures from +21° C to −75° C on both the bond strength and the rubber strength were studied, and these results are shown in tabular form in Tables 2 and 3, respectively, and graphically in Figure 2.

TABLE 2

	21.1° C	0° C	−20° C	−40° C	−50° C	−55° C	−60° C	−65° C	−70° C	−75° C
JA	602	618	637	646	746	919	1210	1731	2554	3135
JB	570	630	640	731	816	926	1084	2025	3645	4342
JC	352	454	575	673	794	836	957	1746	3156	4760
JD	525	580	734	833	960	1001	1105	1921	3280	4336
JE	466	702	823	919	979	991	1059	1670	3590	4264

TABLE 3

	21.1° C	0° C	−20° C	−40° C	−50° C	−55° C	−60° C	−65° C	−70° C
JA	2186	2725	3020	3099	3142	3760	3922	5055	5070
JB	2032	2510	2635	2870	2938	2965	3202	5100	5340
JC	1961	2235	2435	2602	2682	2880	3220	5120	5240
JD	1600	1696	1873	2098	1925	2534	3435	5100	5180
JE	820	975	1073	1175	1344	1770	3380	3525	3530

The variation in rubber strength at low temperatures shows a distinct gradation from the strong rubber JA to the weak rubber JE, similar to the gradation shown by the tensile properties of these rubbers at normal temperatures. The bond strengths of these qualities on the other hand show no definite gradation either at normal or subnormal temperatures. It is evident,

therefore, from a study of these results that the bond strength is in no way dependent on the rubber strength of these stocks.

There is a similarity in the values between −50° C and −75° C within the rubber strength and also within the bond-strength group. This grouping effect appears to be due largely to the loss of elasticity in the rubber which becomes marked between these temperatures. The rubber-strength graphs have a tailing plateau at −65° C to −70° C, which is not noticeable in the bond-strength graphs. It is also noticeable that the graphs for both rubber strength and bond strength at low temperatures have a similarity of shape.

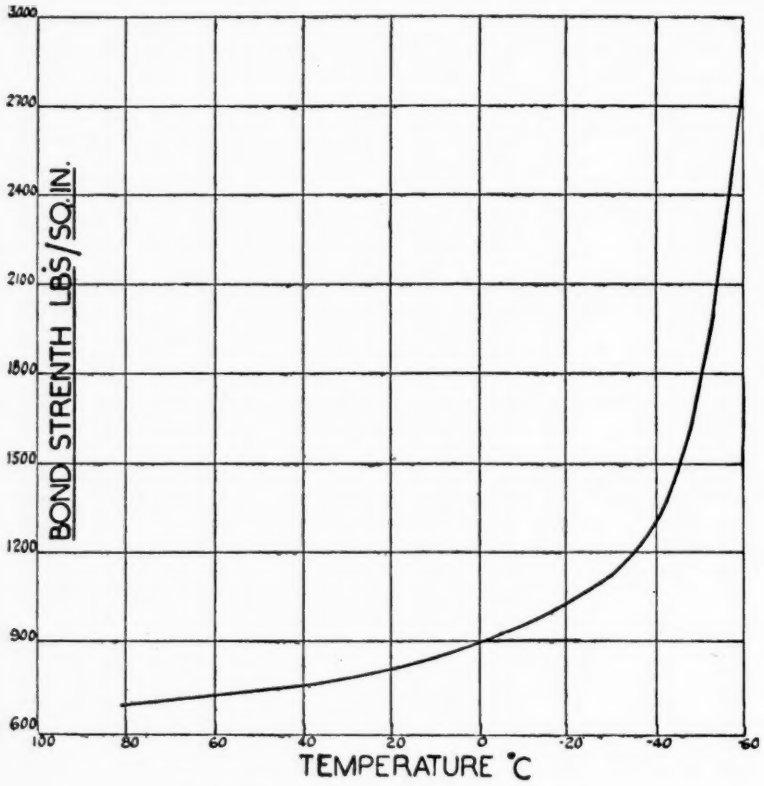


FIG. 1.—The effect of temperature on bond strength.

The same effect is apparent to a lesser extent when a bonded rubber sample is aged, especially during the first seven days after vulcanization. This increase of strength of aging may be due to stiffening of the rubber after vulcanization and perhaps in some small measure to shrinking.

The similarity in the shape of the bond-strength and rubber-strength low-temperature graphs indicated that the increase of bond strength at lower temperatures was possibly a physical phenomenon and connected only with the rubber phase. An investigation of the effect of low temperatures on other physical properties such as tear value, elongation and shape factor was made to see whether these properties might not be correlated with bond strength.

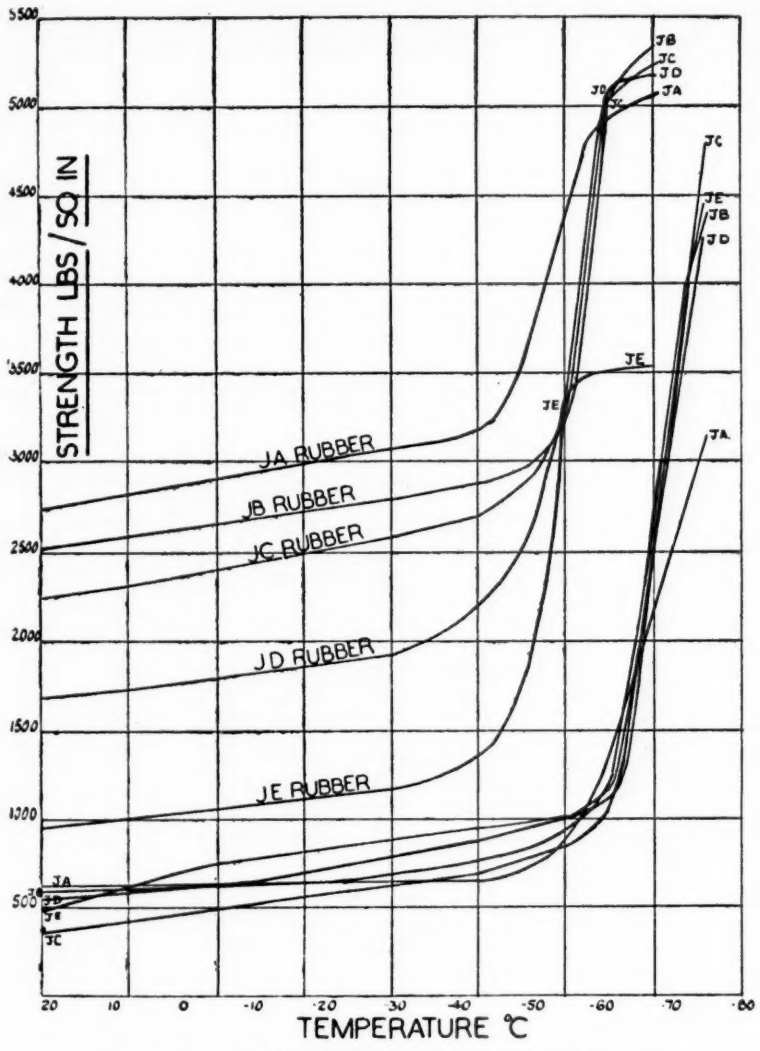


FIG. 2.—The effect of low temperatures on bond and rubber strengths.

TABLE 4

EFFECT ON AGING AT +21° C ON UNITS BONDED WITH NATURAL RUBBER

Time after cure (hours)	2	24	96	168
Average result (lb. per sq. in.)	829	884	998	1096

The effect of low temperatures on the tear value of rubbers JA to JE was determined, using a crescent-shaped test-piece, with a single 0.02-inch cut at the center, pulled on a Scott tensile machine. The results are given in Table 5 and shown graphically in Figure 3.

TABLE 5

EFFECT OF LOW TEMPERATURES ON TEAR VALUE (lb. per in.)

	21.1° C	0° C	−20° C	−40° C	−50° C	−55° C	−60° C	−65° C	−70° C
JA	424	555	580	640	690	800	1125	1404	190
JB	250	320	345	426	540	670	910	1470	315
JC	128	174	185	215	303	440	1180	1320	465
JD	114	155	176	218	312	615	1212	140	270
JE	88	146	159	245	402	920	1075	120	320

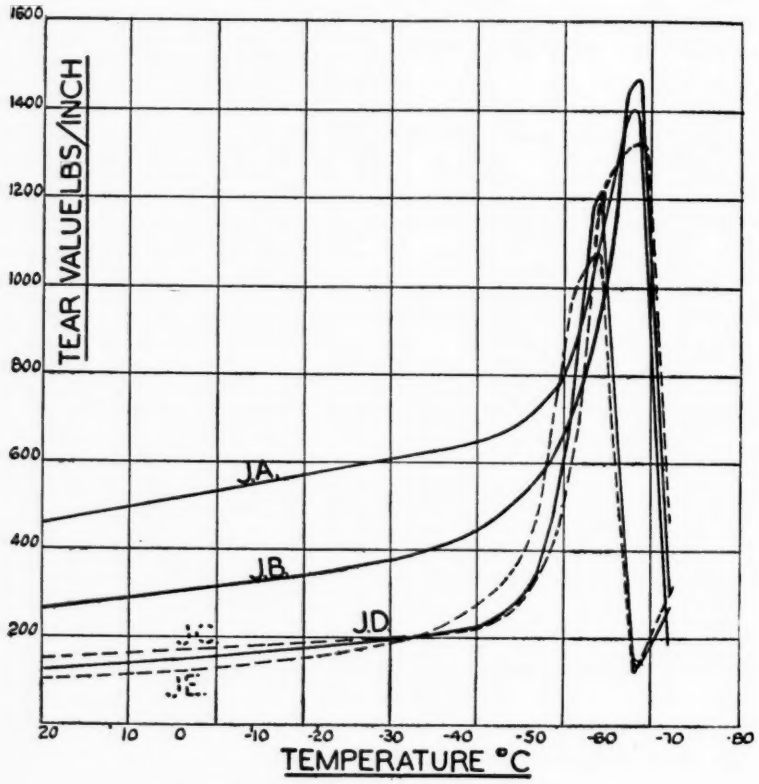


FIG. 3.—Effect of low temperatures on tear strength.

It is evident that the general slope of the curve for tear value against temperature is similar to those of tensile-strength and bond-strength curves shown on Figure 2. It shows an interesting peculiarity in that at a certain stage the sample turns brittle and snaps at a low value. The position of this brittle point varies with different rubbers. JA, JB and JC have their maxima at −65° C and their brittle point at −70° C, whereas JD and JE have their maxima at −60° C and brittle point at −65° C. The brittle point seems to vary with the amount and type of filler used.

The relation between the elongation during pull and at break and the bond-strength was studied in using the small tension mountings illustrated in Figure 4. The results are given in Tables 6 and 7.

TABLE 6

RELATION BETWEEN ELONGATION AND BOND-STRENGTH

Sample	Temp. (° C)	E_B Final elongation (in.)	BS Bond strength (lb. per sq. in.)	$E_B \times BS$
1	21.2	0.807	718	580
2	0	0.686	974	667
3	−25	0.665	1100	732
4	−45	0.724	1245	900
5	−50	0.742	1780	1320
6	−55	0.750	2180	1630
7	−65	0.106	3100	328
8	−75	0.091	4360	398

TABLE 7

Sample	Temp. (° C)	Enduring pull BS at 0.1 in.	0.3 in.	E_B (in.)	BS (lb. per sq. in.)	$E_B \times BS$
1	21.2	145	309	0.755	1129	850
2	0	145	300	0.755	1234	934
3	−20	145	336	0.734	1409	1032
4	−40	163	363	0.704	1409	990
5	−50	254	546	0.782	1830	1455
6	−60	—	—	0.111	1960	218
7	−65	—	—	0.099	2490	271
8	−70	—	—	0.078	2590	225

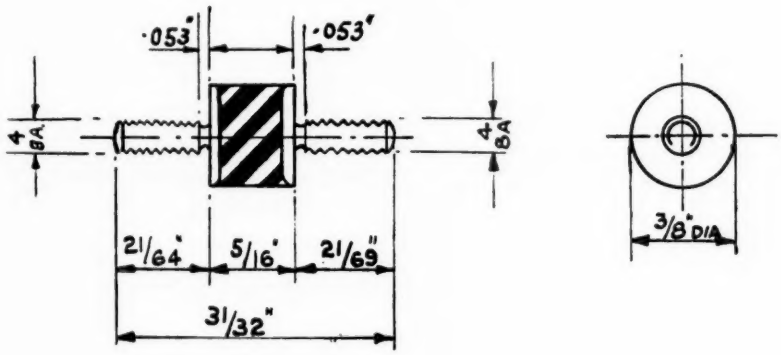


FIG. 4.

The elongation decreases at lower temperatures to approximately 1/10th of its original value, but at constant elongation the bond strength still increases as the temperature is lowered. There appears to be no outstanding relationship between these two properties.

The possibility that the increase of bond strength at low temperatures might be due to the elimination of elongation stresses as the sample grew more rigid was investigated by progressively reducing the rubber thickness between the faces of small, bonded, tension mountings. The reduction of the rubber thickness reduced the elongation during pull as well as the stresses caused by the "necking" effect. A number of tension mountings with rubber thicknesses of 0.190, 0.158, 0.127 and 0.0312 inch were tested. The values are tabulated in Table 8.

TABLE 8

	First experiment			Second experiment	
Rubber thickness (in.)	0.190	0.158	0.127	0.190	0.0312
Average bond strength (lb. per sq. in.)	653	694	635	535	547

It can be seen from these figures that there is no increase in bond strength as the rubber thickness diminishes. Shape is not, therefore, one of the factors causing increased bond strength at low temperatures.

It is evident from a resumé of these physical tests that tensile and tear properties give the same characteristic increase with lower temperatures as bond strength, excepting explicable peculiarities such as the brittle point in the case of tear values. Elongation stresses do not appear to be connected with bond strength and, although elongation is drastically reduced by low temperatures, it bears no proportional relation to the increase of bond strength.

A series of experiments was made the results of which proved definitely that the increase in bond strength at subnormal temperatures was purely a physical phenomenon, independent of any chemical action at the bond and totally dependent on the effect of low temperatures on the rubber structure. Rubber-steel mountings were prepared without brass-plating the metal parts or incorporating any bonding medium whatever. The components were simply moulded together and, after removal from the mould, were maintained in position by surface forces only. The effect of low temperature conditions on these unbonded rubber-metal units was then studied. The results obtained are shown in Table 9A and in Figure 5.

TABLE 9

(*a*) *Effect of decreasing temperature on rubber-steel tension mountings.*

° C	21.5° C	0° C	−20° C	−40° C	−50° C
Bond strength (lb. per sq. in.)	75	—	136	297	545
° C	−55° C	−60° C	−65° C	−70° C	−75° C
Bond strength (lb. per sq. in.)	757	1045	2680	2820	3073

(*b*) *Effect of decreasing temperature on Neoprene GN-steel mountings.*

° C	21.5° C	0° C	−20° C	−40° C	−50° C
Bond strength (lb. per sq. in.)	183	213	409	982	3356
° C	−55° C	−60° C	−65° C	−70° C	−75° C
Bond strength (lb. per sq. in.)	5436	5560	5567	5292	5420

The curves in Figure 5 are similar in character to those obtained in previous experiments. It is evident that the increase in bond strength at lower temperatures is due purely to the alteration of the physical properties of the rubber and not to any chemical effect on the bond. The curves show a tailing-off effect similar to that in the graphs of the tensile-strengths and low-temperatures, but not apparent in the bond-strength graph of rubber bonded to brass-plated units.

Experiments carried out on Neoprene-GN bonded direct to steel mountings showed that a synthetic elastomer reacts similarly, although Neoprene stiffens at higher temperatures and to a much greater extent than natural rubber. As in the previous experiment, there was no bonding agent used between the Neoprene and the steel. The results are tabulated in Table 9 (*b*) and shown graphically in Figure 5. A definite plateau effect is apparent below −50° C, indicating that the Neoprene component has reached its stiffness limit.

In these experiments the increase in bond strength at the bonding interface depends on the effect which low temperatures have on the properties of the particular elastomer which is used.

With both rubber and Neoprene it was observed that maximum bond strengths were developed when the rubbers hardened and lost their resilience.

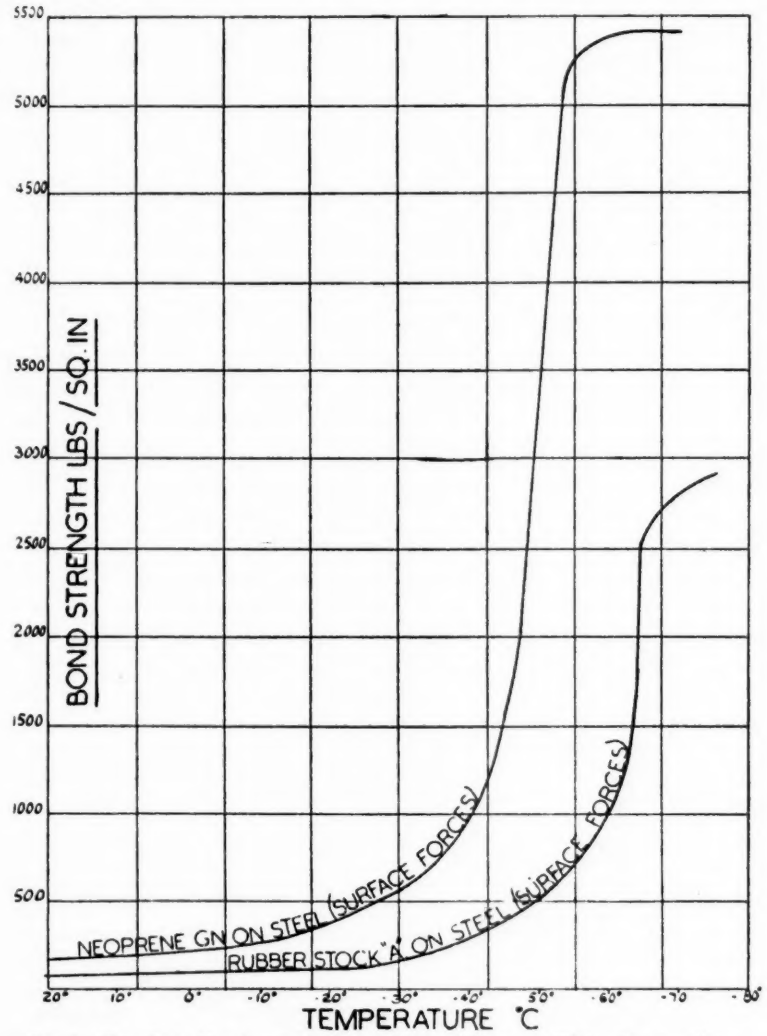


FIG. 5.—The effect of low temperatures on rubber and Neoprene GN tension mountings.

This being the case it was decided that low-temperature tests carried out on an ebonite quality might give interesting results, with some bearing on the general problem.

Investigation of ebonite test units at low temperatures showed that no increase in strength occurred, but a pronounced decrease caused probably by shrinkage of the ebonite away from the outer ring of the test unit used.

TABLE 10

EFFECT OF LOW TEMPERATURES ON EBONITE BONDED UNITS

Temperature (° C)	21.5° C	−55° C	−70° C
Average bond strength (lb. per sq. in.)	1043	753	673

It appears reasonable to assume from these results that the bond developed by ebonite is another manifestation at normal temperatures of the surface tension effect which is apparent with rubber at −65° to −75° C. The hardening in the case of the ebonite, of course, is caused by the chemical action of the sulfur.

It seems evident, therefore, that there are at least two types of rubber-to-metal bond. There is probably a chemical link between brass and rubber, and in certain other cases a bonding effect which appears to be caused by the fixation of surface tension forces.

From experiments on ebonite it appears probable that the ebonite bond is one conforming to this second type, in which the conditions for maximum strength of surface forces are achieved by the nature and hardness of the ebonite.

The crux of the problem lies in the verification of whether the ebonite bond to metal is chemical in nature or a physical one involving surface forces between the ebonite and the metal. In the investigation of this problem a number of ebonite samples were vulcanized on to steel, copper, brass-plated and chromium-plated test units. The results of the tests on these samples are shown in Table 11.

TABLE 11

EBONITE BONDED TO VARIOUS METALS

Metal used	Brass	Copper	Steel	Chromium
Average bond strength (lb. per sq. in.)	1339	204	1320	1228

If the ebonite bond were formed by chemical action, then the values obtained for bond strength would vary with different metals, as the reaction would differ, naturally, from metal to metal. The brass, steel and chromium tests, however, have much the same values for bond strength, and the exposed surfaces of the metals appeared unattacked by the sulfur of the ebonite, being as clear and bright after as before vulcanization. On the other hand the exposed surfaces of the copper parts after vulcanization were well corroded, and those of the ebonite were coated with a fine, blue, powdery layer of copper sulfide and sulfate. The exceptionally low adhesion of copper to ebonite appears to be due to the destruction of the surface tension bond by chemical interaction of the metal with the ebonite. This concept of the ebonite bond was verified further by vulcanizing a pad of ebonite to a smooth, clean, glass plate. The ebonite adhered firmly to the surface of the glass, with which there could only be surface-tension adhesion, and in all tests carried out was practically inseparable. Identical results were obtained by wrap-curing ebonite on to glass tubing.

Tests carried out on the bonding of ebonite to copper-flashed steel revealed that the extent of adhesion obtained depended on the thickness of the coating which was deposited on to the steel. The thinner the deposit the better the adhesion obtained. The following results in Table 12 illustrate this fact.

TABLE 12

EBONITE ON COPPER FLASHED STEEL

Time of dip for copper flash (sec.):	15	30	60	120
Average bond strength (lb. per sq. in.)	1125	313	294	157

The thermoplastic bond developed between rubber and metal by sulfonated rubber derivatives appears to be of the surface tension type also, and depends on the formation of a thin film developing good adhesion to the metal on one hand and miscibility with the rubber on the other. The bonding film being thermoplastic vulcanized samples cannot be removed from the mould while hot without destroying the adhesion. On reheating a cold bonded unit, the bonding agent again becomes plastic and the rubber can be pulled away from the metal, indicating that no chemical action takes place between the sulfonated rubber and the metal. These derivatives can be used for the adhesion of rubber to such articles as glass, concrete, leather, wood, paper and fabrics as well as to ferrous metals (U. S. patent 617,588).

The bond formed by rubber hydrohalides and chlorinated rubbers also seems to fulfil similar conditions, creating the desired strong surface forces by the formation during the vulcanizing process of a hard layer of essentially nonthermoplastic material which is, at the same time, compatible and miscible with natural or synthetic polymers.

Recently, polymers consisting essentially of rubber hydrohalides and halogen-containing rubber derivatives, which usually contain large proportions of sulfur and plasticizers of the dibutyl phthalate type, have come into general use. The characteristics of these products indicate the formation of surface tension bonds. For example, they can be used to unite rubber to glass, porcelain, wood and paper; they are more effective in thin films; metals like copper, manganese and cobalt give poor bonding; the use of greasy or waxy softeners in their manufacture tends to diminish adhesion, and certain external physical conditions such as high humidity, destroy the bond (U. S. patent 2,147,620). Their functioning appears to depend on the surface tension forces developed between the rigid bonding surface and the thin, fairly brittle, thermosetting films, which are also miscible with rubber. In initial experiments, TyPly-R was used as the bonding intermediary between rubber and copper flashed, copper-plated, and zinc-plated steel. Definite signs of reaction were evident between the bonding surfaces of the metals and the TyPly. The copper-flashed units gave an average bond strength of only 415 lb. per sq. in., whereas the copper-plated and zinc-plated samples could be pushed apart by hand. The latter metal reacted to give a blue deposit. The metals, therefore, which do not bond with TyPly-R seem to react either with the sulfur or with the halogen group of the rubber hydrohalide. It seems, therefore, that such bonds are not formed under conditions which tend to destroy the effectiveness of the surface forces.

A number of steel plates, bonded with TyPly and an equal number of brass-plated parts bonded directly to the same rubber compound were subjected to a shock test. A 50-lb. weight was released from a height 12.15 inches on to a circular metal ring 1.08 inches in diameter, placed on the metal back of the bonded plates. Within this circle the TyPly bond was completely destroyed by the shock, whereas the bond obtained by brass-plating was comparatively unaffected. These results are illustrated in Figure 6.

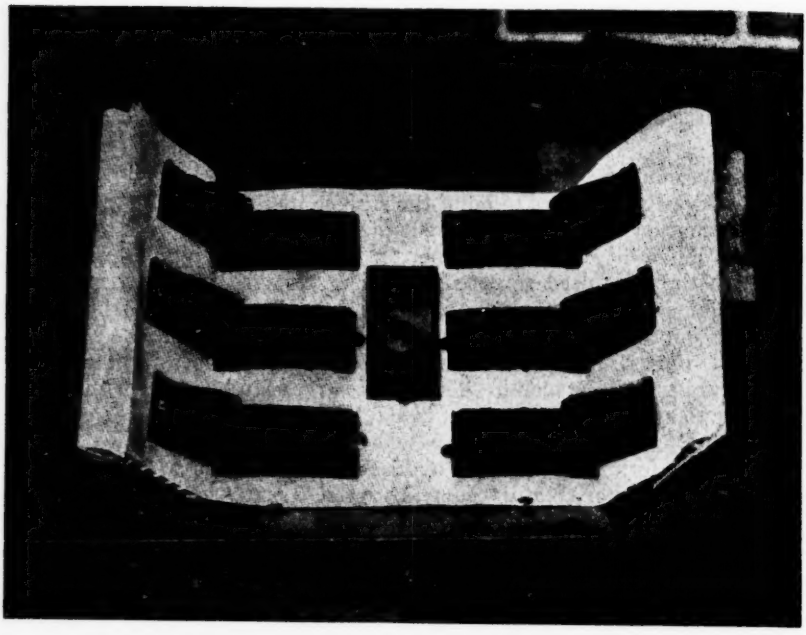


FIG. 6.—The comparative effect of a shock test on two types of bonding.
On left: brass. On right: TyPly-R.

The tensile strength tests were made on bonded dumb-bell tension mountings in which the rubber cross-section was reduced so as to encourage the break to occur in the rubber and not at the bond (Figure 7). All the ebonite and some TyPly tests, as well as those tabulated in Table 1, were made on a circular shear test unit with a metal core and outer ring (Figure 8).

Conclusion.—The results appear to indicate that the greater number of bonding processes used at the present time depend on surface tension forces for their functioning. The processes which can be classified under this type of

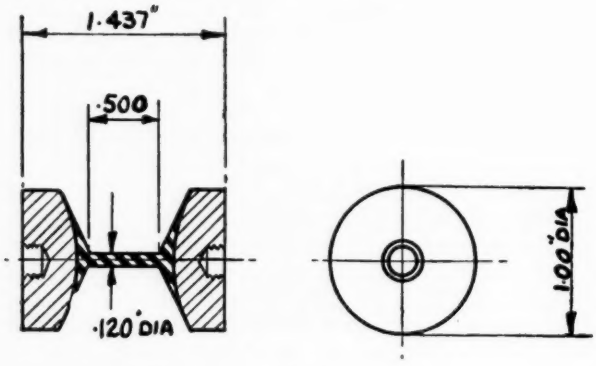


FIG. 7.

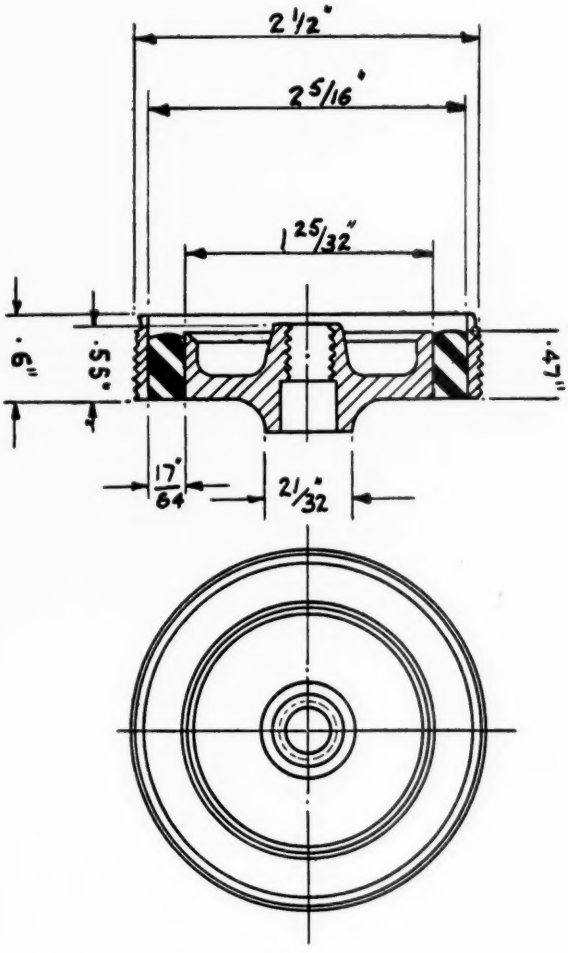


FIG. 8.

physical bond include those using ebonite, rubber hydrohalides, halogen derivatives of rubber and sulfonated rubbers as bonding layers between rubber and metal. This leaves only one major process, which can be quoted as an example of chemical bonding, and that is the direct union of rubber with electrodeposited brass of known composition.

ACKNOWLEDGMENT

Acknowledgment is made to the Andre Rubber Company for permission to publish this paper.

CHEMICAL NATURE OF THE RUBBER-TO-BRASS BOND *

S. Buchan and W. D. Rae

Introduction.—The need for incorporating rubber into machinery to reduce vibration has led to the development of methods for uniting rubber with more rigid materials, in particular with metals of all types. Several methods are in use today, new ones are being developed and old methods improved. Theoretically two types of union are possible, the first, one in which the rubber and metal are held together by physical forces; the second, a chemical union. In practice, however, it is more convenient to divide them into three classes. (1) adhesives, (2) surface tension bonds, and (3) chemical bonds.

Adhesives cover for the most part methods for uniting vulcanized rubber to metal. They depend on the presence between the rubber and the metal of a layer of cement which is plastic and flows when in solution, but when dried sets to form an elastic intermediate layer. Such cements usually have a rubber base.

In the second class are the sulfonated rubbers, chlorinated rubbers, Ty-plys, and other patented cements for bonding rubber to metals during the curing process. The method which depends on the presence of an intermediate layer of ebonite between rubber and metal also comes into this class. This type of union is being dealt with in a paper by Buchan and Shanks[1]. It is established, for example, that it is caused by surface tension forces, and demonstrates that such a union can be destroyed by shock-loading.

The third type of union, the chemical, which is dependent in effect on interatomic linkages between the rubber and the metal, does not suffer from this disadvantage and, if properly controlled, would be expected to produce better and more consistent bonding. Only one of the methods in use today appears to satisfy this condition. The process referred to depends on the bonding properties of a layer of electrodeposited brass between rubber and metal. Although it has been accepted generally that the union obtained by this means is chemical, no comprehensive theory has been put forward to account for the mechanism of the bond, although it has been apparent for some time that the full possibilities of the method cannot be exploited until a better understanding of the process is obtained.

The brass-plating method was one of the earliest in use and for many years was a process conducted largely on an empirical basis, but the importance of the rubber-metal unit in engineering, and the development of alternative methods of bonding, has intensified efforts to improve the technique and discover more about the fundamental reactions. It has been placed now on a more scientific foundation, largely as a result of this work.

Investigations, however, have been concentrated more on improvement of technique rather than on enquiry into the fundaments of the chemical reactions. The tendency has been to treat the brass and the rubber as separate items, and

*Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 21, No. 5, pages 323–342, February 1946.

no correlation has been sought between the two. This is unsatisfactory, as can be seen from the fact that at the present time, brasses with a copper content varying from 68 to 80 per cent can be bonded satisfactorily, the type of rubber stock used varying just as widely.

To get the optimum bonding effect, a different composition of rubber is required for each type of brass, indicating that they are interrelated and that they should be dealt with together.

Some of the work done, however, has proved useful as a basis for further investigation. On the brass side a paper by Ferguson and Sturdevant[2] stands out as the most valuable contribution. Here many of the factors which contribute to giving a brass which is both uniform and consistent are evaluated. On the rubber side attention has been directed towards a qualitative study of the effect of various compounding ingredients in the rubber on adhesion. McCortney[3] was the most outstanding contributor in earlier years. Later, Buchan[4] established that sulfur is a necessary reactant in bond formation.

PART I

Theoretical Aspect.—There are four possible reactants which may take part in bond formation, all four always being present at the brass-rubber interface, *viz.*, copper, zinc, sulfur and rubber. The other ingredients vary widely, sometimes appearing to be essential constituents of the compound, at other times not required. From published experimental data it has been decided that these latter ingredients affect bond formation only by influencing to a limited extent the course of the major reaction, *i.e.*, between the brass on the one hand and the sulfur and rubber on the other hand. Further work done on this aspect of the problem has been omitted, therefore, to simplify the picture.

Sulfur has already been isolated as one essential constituent of the bond. It is known also, that the three remaining constituents react readily with sulfur, the copper and zinc to form sulfides of these metals, the rubber to give the vulcanized product. Copper and copper compounds are notable for the deleterious effect which they have on rubber; moreover, a bond can be obtained between rubber and pure copper. Zinc compounds on the other hand have no such bad effect, and it is difficult, if not impossible, to bond zinc directly to rubber. It would appear logical to assume, therefore, that in bonding brass the copper constituent is the active agent, with the zinc exerting a measure of control over the reaction.

Satake[5] has studied in detail the reactions of copper with sulfur compounded into rubber, and reached the following conclusions.

The corrosion curve is parabolic in the initial stages, and can be expressed by the equation:

$$x = Kt^n$$

x = amount of copper in grams which reacts.
t = the time of vulcanization.
K and n are constants for the rubber mix being studied.

Only the free sulfur in the rubber had an appreciable effect on the amount of corrosion, sulfur combined with the rubber reacted very slowly. Increase in the free sulfur and decrease in the accelerator content both increased the amount of corrosion.

Copper, being one of the transition elements, possesses a variable valency and can, therefore, form more than one chemical compound with the same element. Thus, two stable sulfides are known to be formed, cuprous sulfide (Cu_2S) and cupric sulfide (CuS). Satake[5] found in his experiments with rubber and copper that both were formed, the amounts being always in the ratio of 5 parts cuprous sulfide to 3 parts cupric sulfide.

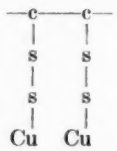
Fischbeck and Dorner[6] have demonstrated that sulfur in carbon disulfide solution reacts briskly with copper powder to give wholly cuprous sulfide, and the subsequent taking up of additional sulfur occurs with a small measurable velocity. This velocity is governed by the rate of diffusion of the sulfur through the layers of the cupric sulfide, and this diffusion rate is controlled by the concentration of sulfur and the temperature at which the reaction takes place[7]. In any reaction between sulfur and copper, therefore, it would appear that the lower sulfide is always formed first.

This lower sulfide has several reactions open to it: (1) it can link itself to a "free" sulfur atom to form cupric sulfide; (2) it can attach itself to a sulfur atom already linked to the rubber; (3) it can attach itself directly to the rubber at one of the points of unsaturation.

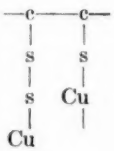
Reaction (1) takes place to an appreciable extent only when there is an excess of uncombined sulfur.

Reaction (2) can take place at all concentrations of sulfur, but when there is excess present there is an added tendency for formation of sulfur chains between the copper and the rubber.

I.



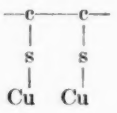
II.



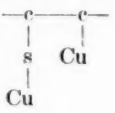
From a stereochemical point of view, structure II is less likely than structure I; hence the greater probability of sulfur-sulfur linkage. The strength of these chains is not great by nature of the chemical forces creating them, and the longer the chain the weaker is the linkage. Thus, if reaction (2) should occur, weak bond formation is likely to result.

With reaction (3), however, the two possible structures are:

III.



IV.



and either reaction, if it should take place, is likely to yield a satisfactory bond. Again, stereochemically structure III is more probable than structure IV. It can be seen, therefore, that less sulfur is required to enter into combination with the copper in reaction (3) than in reactions (1) and (2), and that, consequently, bad bonding brasses will be characterized by excessive sulfide formation. By the same reasoning, reaction (2) is more likely to occur when fast-curing stocks are vulcanized against brass, because of rapid saturation with sulfur of the reactive double bonds.

GENERAL SCHEME

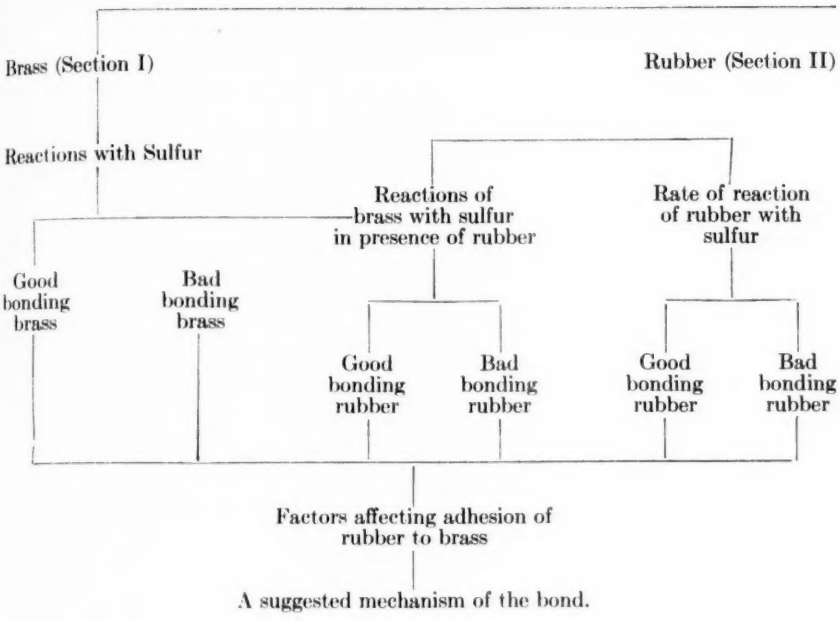

Brass (Section I)
Rubber (Section II)
Reactions with Sulfur
Reactions of brass with sulfur in presence of rubber
Rate of reaction of rubber with sulfur
Good bonding brass
Bad bonding brass
Good bonding rubber
Bad bonding rubber
Good bonding rubber
Bad bonding rubber
Factors affecting adhesion of rubber to brass
A suggested mechanism of the bond.

FIG. 1.

PART II

Experimental.—The general scheme adhered to is outlined in Figure 1.

Experience in the bonding of brass to rubber has led to a logical separation of rubber stocks into those which bond and those which do not. It was a comparatively simple matter, therefore, to choose samples of each type of rubber stock for investigation. In the case of the deposit, however, the production of good and bad-bonding brasses at will was not so easy. However, two newly discovered factors have been made use of.

A plating solution which has been made up afresh fails to give a good bonding deposit, although the composition and appearance of the brass, etc., are within the prescribed limits. If electrolysis of the solution is continued, however, a satisfactory brass deposit is obtained eventually.

Chemical examination of the solution during this period revealed a change in the amount of sodium cyanide combined with the copper cyanide. In the initial stages the ratio of molecules of cyanide combined with copper to the molecules of copper was in the region of 2.6. That is, there was present a mixture of the two sodium cuprocyanide complexes, $NaCu(CN)_2$ and $Na_2Cu(CN)_3$. The ratio gradually increased as electrolysis was continued until the value of the ratio exceeded 3. From this point onwards good bonding brass was obtained consistently from the plating solution.

It was noted on several occasions, when failure to obtain adhesion was encountered in production, that the above mentioned ratio had fallen below 3, and that bonding brass was not obtained until such time as the ratio regained its original value.

A specially prepared solution was taken and brought into a stable condition in the manner already described, *i.e.*, by continued electrolysis. Copper sulfate solution was then added to this solution until the cyanide to copper ratio was reduced to 2.7. Test-plates were taken from the bath before and after addition, and it was noted that the introduction of copper sulfate led to a definite loss of adhesion. This procedure was repeated three times with the same result. Test results are shown on Figure 2. Each row of plates comprised one series of experiments, the plates being taken from the bath in order from right to left. First appearance of nonadhesion in each series coincided with the reduction of the cyanide ratio by the addition of copper sulfate.

x-Ray examination of the two types of brass produced showed that the bad brass was nonuniform in structure, whereas the good brass was uniform[8].

These two types of brass were used to study the reactions which occurred at the brass surface when in contact with a rubber-sulfur mix at vulcanizing temperatures, *viz.*, 150° C. These, together with experiments to measure more directly the corrosive effect of sulfur on the two types of brass, form the substance of Section I.

Section I.—In these and subsequent experiments the amount of sulfide formed had to be measured. It may be advisable, therefore, at this point to describe the apparatus and method employed in this estimation.

Apparatus.—The apparatus consisted of a flask fitted with a gas inlet, a dropping funnel and an outlet leading to a condenser held in a vertical position. A glass tube from the top of the condenser was connected to one arm of a U tube, which served as an acid trap, the other arm being linked with three gas-washing bottles. Ground glass joints were used wherever possible; elsewhere sulfurless Neoprene tubing was employed to hold the glass connecting tubes in close contact and to prevent the escape of gases.

Method.—25 cc. of 30 per cent sodium hydroxide solution (A. R. Grade), was placed in each of the gas washing bottles. A sample, the sulfide content of which was to be measured, was introduced into the flask, and the whole apparatus swept clear of air by passing a stream of pure nitrogen through it for 10 minutes. The nitrogen, obtained from a cylinder, was purified by passing it first through an alkaline solution of pyrogallol and then through a 10 per cent solution of sodium hydroxide. 100 cc. of distilled water was introduced into the flask through the dropping funnel. This was followed by 100 cc. of a 10 per cent solution of stannous chloride (A. R. Grade), dissolved in concentrated hydrochloric acid (A. R. Grade sp. gr. 1.18). The solution was boiled until all metallic constituents had passed into solution. This took usually from 30 minutes to 2 hours, depending on the nature of the sample being analyzed. Differences in experimental procedure which had to be adopted from one series of experiments to another are listed when the experiments themselves are described. During the course of the experiment, pure nitrogen was passed continuously through the apparatus. The purpose of the stannous chloride was primarily to cause reduction of the copper sulfide to cuprous chloride and hydrogen sulfide, and, secondly, to prevent oxidation of the sulfide.

The gas-washing bottles and the U tube were disconnected and their contents washed into a beaker, the sulfide being oxidized to sulfate by the addition of brominated hydrochloric acid. After the solution had been made acidic by further addition of hydrochloric acid, excess bromine was boiled off. A few cc. of picric acid dissolved in hydrochloric acid was added, and the sulfate precipitated by the addition of 10 cc. of barium chloride (10 per cent solution A. R.

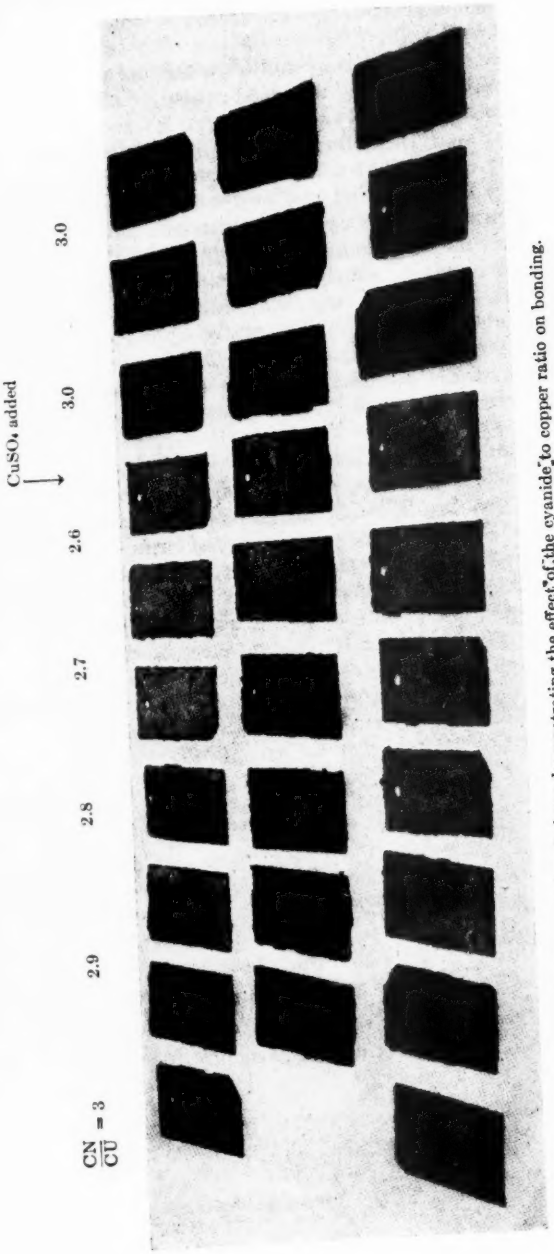


FIG. 2.—A series of plates demonstrating the effect of the cyanide to copper ratio on bonding.

Grade). After allowing to stand for three hours the solution was filtered. The precipitate was washed thoroughly, ashed and weighed as barium sulfate.

Action of a Rubber-Sulfur Mix on Brass.—The two types of brass already mentioned were used to study the reaction which occurred at the surface when in contact with compounded unvulcanized rubber at 150° C. For this purpose, the brass layers were deposited on aluminum plates. Aluminum was used as the basis metal for analytical convenience, since the variable sulfur content of steel rendered any subsequent sulfide determination valueless. These plates were coated with a rubber-sulfur mix let down in benzene, no other ingredient being present. On top of this cement was placed a pad of vulcanized rubber to reproduce as nearly as possible actual bonding conditions. Plates built up in this way were cured in a hydraulic press for times ranging from 5 to 20 minutes. At the end of these periods of cure, the plates were removed and the prevulcanized rubber pads stripped off. The plates were then immersed in benzene, whereupon the partially vulcanized rubber cement became detached, leaving exposed the brass surface covered with the reaction product.

The plates were cut up and placed in the sulfide-measuring apparatus to determine the amount of sulfide formed on the surface.

The first rubber mix tried contained 10 per cent sulfur. Extensive corrosion occurred in all experiments, a powdery deposit being obtained with both good and bad brass, and no conclusions could be derived from the experimental results. On reducing the percentages of sulfur to 5 the bad brass again yielded a powdery deposit, and the results were still erratic, although some idea of the order of the degree of corrosion was obtained. During the first five minutes for example, about 5.04×10^{-5} g. sulfur reacted with each sq. cm. of brass. With the good bonding brass, however, more consistent figures were obtained, and these are given below. For comparison, similar figures which were obtained from a deposit taken from a solution which had been in production for 4 months are also given.

TABLE 1

Cure t (min.)	Weight of sulfur (g. per sq. cm. $\times 10^{-5}$)	
	Good brass $\times$	Production brass $\times$
5	1.742	1.920
10	3.255	3.755
15	4.170	5.250

The amount of sulfur in the mix was reduced to 2.5 per cent in an effort to obtain more reliable figures for the amount of sulfide formed with bad brass, but even with this low sulfur content, a loose powdery deposit was obtained.

The figures for the good brass obtained in this series of experiments are reproduced below:

TABLE 2

Cure t (min.)	Weight of sulfur (g. per sq. cm. $\times 10^{-5}$)	
	Good brass $\times$	Production brass $\times$
5	2.330	1.614
10	2.732	2.668
15	3.403	3.972

These figures demonstrate, if only qualitatively, that sulfide formation is greater in the case of the bad bonding brass and, secondly, that the amount of corrosion depends on the amount of sulfur in the mix. This latter conclusion confirms those obtained by Satake[5] in his experiments on the corrosion of copper. The effect of the presence of the zinc is also made evident by comparing figures obtained by Satake for copper with those obtained for brass, which are given above. Satake's values were 4.65×10^{-3} gram of sulfur per sq. cm. for an unaccelerated mix containing 5 per cent sulfur, 3.72×10^{-3} gram of sulfur per sq. cm. for an accelerated mix containing 0.5 per cent diphenylguanidine and 2.48×10^{-3} gram of sulfur per sq. cm. for a mix containing 1.5 of diphenylguanidine. The accelerated mixes also contained 5 per cent of sulfur. These figures are for a 15-minute cure. The zinc appears to act as a diluent in reducing the rate and the amount of reaction occurring between the copper and the sulfur.

Comparison of the Corrosion by Sulfur of the Two Types of Brass.—It has been indicated that good bonding brass does not corrode so rapidly as bad bonding brass. This behavior was not entirely unexpected, as x-ray and electronmicroscopic examination have led us to believe that bad bonding brass is less uniform in structure. To confirm this finding, it was decided to study in a more direct manner the behavior of the two types of brass towards sulfur. The following method was found to be satisfactory and was adopted.

Brass was deposited on sheets of tin-foil measuring 12×6 inches under conditions which were arranged so as to give good and bad bonding deposits. The central portions measuring 10×5 inches were taken and cut into sections 5×2 inches in area. Each section was placed in a 12-inch long Carius tube along with a saturated solution of sulfur in acetone, containing excess of sulfur to the extent of 0.5 gram. The tubes were sealed and placed in an air oven at 150° C. One was removed every 5 minutes for each type of brass examined. The seal was broken and the foil carefully removed. The tin-foil which had been weighed before placing in the tube was now measured carefully and all adherent sulfur removed from the surface by extraction with acetone in a Soxhlet apparatus. The foil was then weighed again. The foil was placed in the sulfide estimation apparatus and the sulfide estimated in the manner already described. The increase in weight of the foil corresponded to the amount of sulfide found to be combined with the brass, indicating that no other reaction products had been formed. The results are given in Table 3. The bad brass was produced from a plating solution which had been modified by addition of copper sulfate as already described. The "fair" brass was plated from a solution which had been in normal production for several months, but which, at that particular time, was giving indifferent bonding results.

These results are graphed in Figure 3, and confirm those obtained in the preceding series of experiments.

A similar set of experiments was now run, taking samples of the brass deposit at intervals from a freshly prepared plating solution as adhesion was gradually being obtained by means of continued electrolysis. The results are given in Table 4.

These results are graphed in Figure 4. Again, they confirm those already obtained.

Satake[5] obtained a flattening of the curve at the higher cures. This he found to coincide with the disappearance of free sulfur in the rubber in the vicinity of the copper. Such an effect cannot occur in the experiments just described, for the concentration of sulfur in the acetone was maintained con-

TABLE 3

Time in oven (min.)	Area (sq. cm.)	Increase in weight of foil (g.)	Weight of sulfur cal. from $BaSO_4$ (g.)	Weight of sulfur (g. per sq. cm. $\times 10^{-5}$)
Good brass				
10	95.80	0.0016	0.0016	1.67
15	99.72	0.0023	0.0022	2.31
20	99.72	0.0025	0.0025	2.76
25	93.85	0.0024	0.0024	2.54
30	89.98	0.0023	0.0023(5)	2.55
Fair brass				
15	114.06	0.0038	0.0038	3.33
20	116.36	0.0040	0.0041	3.52
25	128.61	0.0046	0.0046	3.58
30	115.36	0.0073	0.0068	5.89
35	112.26	0.0087	0.0084	7.46
Bad brass				
15	138.03	0.0041	0.0041	2.97
20	137.64	0.0061	0.0060	4.36
25	130.96	0.0081	0.0081	6.25
30	139.00	0.0084	0.0080	6.22

stant. The flattening of the curves in this case is probably due to the presence of zinc; the more uniformly it is distributed the greater, of course, will be its screening effect.

These results appear to justify the conclusion that heavy sulfide formation is one of the prime causes of bad bonding between rubber and brass deposits.

Section II. A Comparison of Good and Bad Bonding Stocks.—As already mentioned, experience in the production bonding of rubber to brass has led to a

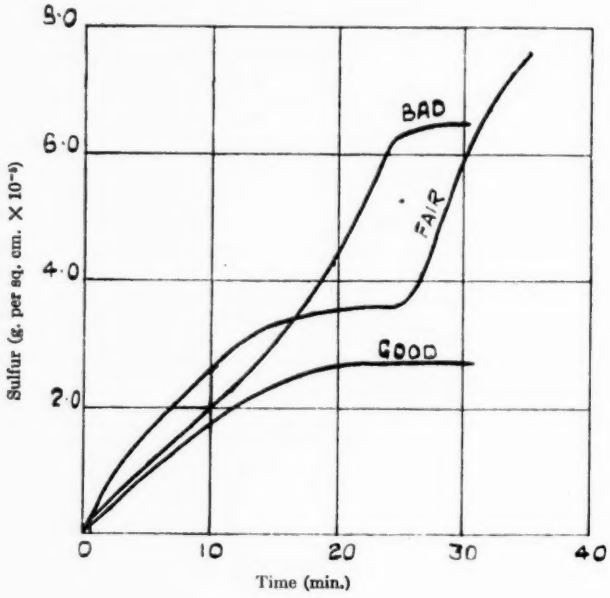


FIG. 3.

TABLE 4

Time in oven	Area (sq. cm.)	Increase in weight of foil (g.) Time (min.)	Weight of sulfur cal. from $BaSO_4$ (g.)	Weight of sulfur (g. per sq. cm. $\times 10^{-6}$)
1st plating.	Adhesion nil			
10	96.59	0.0015	0.0015	1.55
15	97.20	0.0019	0.0023	2.37
20	126.16	0.0056	0.0058	4.60
25	99.07	0.0116	0.0117	11.78
30	95.33	0.0137	0.0137	14.32
12 hours later.	Adhesion nil			
10	116.75	0.0016	0.0018	1.47
15	114.17	0.0021	0.0027	2.36
20	106.43	0.0040	0.0045	4.23
25	113.00	0.0072	0.0075	6.64
30	126.94	0.0088	0.0095	7.52
Adhesion good				
10	137.77	0.0018	0.0019	1.28
15	137.13	0.0016	0.0016	1.16
20	138.06	0.0031	0.0031	2.23
25	115.58	0.0027	0.0028	2.33
30	115.58	0.0020	0.0024	1.73

natural division of rubber stocks into those which bond well and those which bond badly. A study has been made of the behavior of these stocks towards brass possessing good bonding characteristics, and the amount of sulfide formation in each case measured. For the sake of analytical convenience, a means had to be found for separating the brass from the basic metal. As an adherent

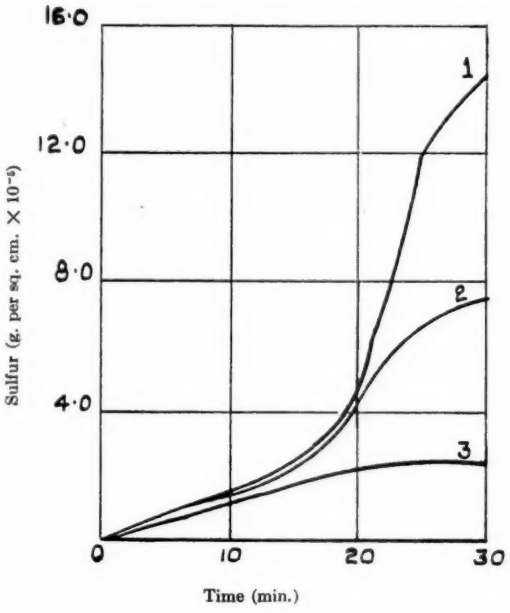


FIG. 4.

deposit is not obtained when stainless steel is brass-plated under normal conditions, this suggested a means of separating the brass and the rubber layers from the basic metal after cure. The stocks used are listed below in Table 5, only the essential curing ingredients being given.

Stainless steel plates measuring 4 × 2 inches were brass-plated for 20 minutes, then washed and dried. A sheet of rubber $\frac{1}{4}$ inch thick was moulded in contact with the deposit and, after cure was stripped off, taking with it the brass layer. The dimensions of the pad were measured accurately and it was then placed in the sulfide-estimating apparatus.

A two-cavity mould was used, a control of the same stock being moulded in the second cavity. The amount of sulfide on the surface of this control was estimated in the same way.

TABLE 5

Stock	A	B	C	D	E	F	G
Rubber	100	100	100	100	100	100	100
Mercaptobenzothiazole	.45	1.0	1.0	0.5	—	.60	.60
Diphenylguanidine tartrate	.30	—	—	—	—	.40	.40
Diphenylguanidine	—	—	0.25	—	—	—	—
Tetraethylthiuram disulfide	—	—	—	3	4	—	—
Vulcaplas	—	—	—	—	—	5	—
Novoplas	—	—	—	—	—	—	5
Sulfur	2.5	2.5	2.5	—	—	—	—

From this the amount of sulfur which reacted with the brass was calculated.

The following results were obtained.

TABLE 6

Experiment		Area (sq. cm.)	Weight of $BaSO_4$ (g.)	Weight of sulfur (g. per sq. cm. × 10^{-5})
Stock (A)	Adhesion good			
1	*A*	46.50	0.0427	12.63
	B	49.10	0.0432	11.28
2	*A*	31.60	0.0338	14.76
	B	50.90	0.0539	14.48
3	*A*	32.09	0.0374	15.95
	B	31.23	0.0358	15.67
Stock (B)	Adhesion good			
1	*A*	44.80	0.0315	10.55
	B	49.10	0.0315	8.82
2	*A*	46.50	0.0292	8.65
	B	49.50	0.0302	8.41
3	*A*	34.56	0.0393	15.63
	B	23.41	0.0211	12.36
Stock (C)	Adhesion bad			
1	*A*	47.73	0.0475	13.67
	B	48.38	0.0464	13.13
2	*A*	34.96	0.0514	20.00
	B	47.02	0.0303	9.73
3	*A*	47.73	0.0644	18.56
	B	48.38	0.0564	16.20
Stock (D)	Adhesion bad			
1	*A*	47.65	0.0637	17.81
	B	48.80	0.0317	5.55
2	*A*	48.80	0.0256	6.97
	B	48.80	0.0129	3.51
3	*A*	47.76	0*M*0302	9.97
	B	50.45	0.0320	8.44

TABLE 6—*Continued*

Experiment		Area (sq. cm.)	Weight of $BaSO_4$ (g.)	Weight of sulfur (g. per sq. cm. $\times 10^{-5}$)
Stock (F)	Adhesion good			
1	*A*	33.56	0.0940	38.53
	B	29.51	0.0914	32.45
2	*A*	32.02	0.0719	30.42
	B	30.55	0.0396	17.94
3	*A*	34.00	0.0851	33.16
	B	31.43	0.0746	31.09
Stock (G)	Adhesion bad			
1	*A*	49.02	0.0672	18.83
	B	49.02	0.0226	6.37
2	*A*	50.40	0.0767	21.05
	B	49.02	0.0510	14.31
3	*A*	50.95	0.0646	17.42
	B	46.50	0.0424	12.57
Stock (H)				
1	*A*	40.58	0.0957	25.73
	B	38.69	0.0718	25.52
2	*A*	35.54	0.0848	34.38
	B	31.42	0.0737	32.26
3	*A*	32.03	0.0637	27.43
	B	31.42	0.0829	23.55

* *B* signifies control in each case.

In all cases the value obtained for the brass layer was higher than that obtained for the control. If we assume that no attack, or at the most only slight attack, occurs on the sulfur combined with the rubber, the value we obtain for the control is due to free sulfur and sulfur present on the surface in the form of zinc sulfide, etc. As the presence of the brass layer always causes an increase in the measurable sulfide formation, it is not unlikely that this occurs at the expense of the sulfur combined with the rubber. In stocks A and B, the results are reasonably consistent, but in Stock C, a wide variation in the amount of sulfide formed occurs. To confirm whether this was a true picture a second series of experiments were run on Stock C. The results are tabulated below.

TABLE 7

STOCK (C) ADHESION BAD

Experiment		Area (sq. cm.)	Weight of $BaSO_4$ (g.)	Weight of sulfur (g. per sq. cm. $\times 10^{-5}$)
1	*A*	33.25	0.0492	20.34
	B	30.45	0.0323	14.56
2	*A*	33.60	0.0399	16.39
	B	30.45	0.0332	14.94
3	*A*	33.00	0.0551	22.96
	B	29.28	0.0311	14.57
4	*A*	33.00	0.0313	13.04
	B	30.00	0.0263	12.03

The figures are reproducible and, therefore, in Stock C, it is evident that the amount of sulfide formed varies from sample to sample and probably over the same sample. It would be expected that when the amount of sulfide formed is of the same order as in Stocks A and B, a good bond will be obtained, but when the sulfide formed is considerably higher, a bad bond would be more likely. If this hypothesis is correct, then Stock C should exhibit a large variation in bonding properties. To establish this, twelve bonded units were

moulded, using Stock C. The units consisted of two concentric rings, bonded together by means of the rubber under test. A further twelve units were moulded, using a standard good bonding rubber stock. All metal parts were plated at the same time in the same plating solution and were moulded under the same conditions, two of each type of rubber being cured simultaneously in the same press. The units were tested in shear. The results obtained are tabulated below in Table 8.

TABLE 8

Stock C Adhesion in lb. per sq. in. on inner ring after cure of 25 min. at 150° C	Stock AD.27 Adhesion in lb. per sq. in. on inner ring after cure of 25 min. at 150° C
09	662
11	960
10	815
13	883
12	834
519	834
13	1000
10	740
844	730
441	1088
14	1385
327	673

By averaging the results in Tables 10 to 17, the effect of variations in the rubber and the brass can be reduced to a great extent. These average results are tabulated below.

TABLE 9

Stocks	Brass layer (g. per sq. cm. $\times 10^{-4}$)	Control	Difference	Adhesion
A	14.45	13.81	0.64	Good
B	11.61	9.87	1.74	Good
C	17.41	12.68	4.73	Bad
D	11.58	5.83	5.73	Bad
F	34.02	27.16	6.86	Good
G	19.10	11.06	8.04	Bad
H	31.39	27.11	4.28	Good

In qualities A, B, and C, that is, the straight sulfur-accelerator stocks, the good bonding rubbers are characterized by low sulfide formation, whereas the bad bonding one forms considerably more sulfide. The major difference in the compounding of these stocks is that in A and B a delayed-action accelerator is used, in this case a mixture of mercaptobenzothiazole and diphenylguanidine tartrate, while in Stock C the diphenylguanidine is present, uncombined, along with mercaptobenzothiazole. The combination of the acid and alkaline accelerators produces a speeding up of vulcanization in the initial stages of cure. It will be demonstrated later, when the experiments on the rate of reaction between rubber and sulfur are carried out, that this makes reaction (3) less probable and reaction (1) and (2) more probable.

With Stock D, the tetraethylthiuram disulfide-accelerated, high sulfide formation again occurred and no bond resulted. As the high values obtained for sulfide formation were rather difficult to account for, it was suggested that chemical action may have taken place between the brass deposit and the tetraethylthiuram disulfide and that the reaction products were included in the results. Tests to confirm this possibility were put in hand. When samples of

copper foil were placed in a solution of tetraethylthiuram disulfide in benzene, a deposit formed on the surface of the metal. This deposit dissolved in chloroform and on evaporation, the copper complex of tetraethylthiuram disulfide was left. This compound would tend to hinder any reaction between the brass and the rubber. Such a compound, too, would yield hydrogen sulfide by the action of hydrochloric acid and stannous chloride, and would account in some measure for the high values obtained in the sulfide estimation.

Of the two other natural rubbers tested, stock F bonded well, whereas stock G did not, despite the fact that sulfide formation was approximately the same in each case. The amount formed was considerably higher than was obtained with any of the other stocks. It is thought that the presence of the ingredients Vulcaplas and Novoplas may have some bearing on this difference. The effect of these two compounding ingredients on the reaction between the rubber and sulfur was found to be somewhat similar, this being confirmed by direct measurement of their rates of reaction.

The structures involved are as follows:

Vulcaplas $(CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_2—S_4—)_x$

Novoplas $(CH_2—CH_2—O—CH_2—O_2—CH_2—CH_2—CH_2—CH_2—S_4)_x$

The radicals —CL—OH and —SO_3H are known to assist the bonding of rubber to metal and are used in many patented cements for this purpose. Secondly a Neoprene stock (Stock H) examined also gave good adhesion, despite the fact that a considerable amount of sulfur was present at the bonding interface. Its structure is similar to that of Vulcaplas in that it possesses an active radical, in this case chlorine:

$$—CH_2—\underset{\displaystyle Cl}{\underset{|}{C}}=CH—CH_2—CH_2—\underset{\displaystyle Cl}{\underset{|}{C}}=CH—CH_2—$$

The action of these radicals —Cl, —OH, and —SO_2H is probably that of assisting chemical reaction at the adjacent carbon atoms. This may account for the failure of a Novoplas stock to bond where the others succeed in doing so, since Novoplas possesses no such radical. There is a second possibility, although it must be judged to be of only minor consequence. Rupture of these structures can be expected to take place readily at the sulfur bonds, with the production of fresh points of linkage with the brass.

The Rate of Reaction of Sulfur with Rubber.—It has been observed that bonding between rubber and brass occurs early in the curing cycle and interest is centered, therefore, on the rate of reaction during the initial stages of vulcanization. The usual method of following the rate of combination of sulfur with rubber was adopted by determining the amount of uncombined sulfur left in the rubber at various stages throughout the cure. Standard methods for estimating the free sulfur could not be used, however, because all required heating the rubber for a further 2 to 8 hours at elevated temperatures, which would have introduced a large error into each test. It was necessary, therefore, to devise a method which called for no further heating of the rubber after the vulcanizing treatment.

The rubber stock to be examined was sheeted out to a thickness of 1/16 inch, and eight rectangular sections were cut out, each weighing approximately

1 gram. They were carefully wrapped in tin-foil, care being taken to ensure that no air bubbles were entrained. These test-pieces were then suspended in a solution of ethylene glycol maintained at a temperature of 120° C. The solution was kept in constant motion by means of a stirrer, and one sample was removed every minute. Each of these samples, after removal, was cut up into

TABLE 10

Weight of rubber (g.)	Time of cure (min.)	Weight of $BaSO_4$ (g.)	Sulfur (per cent)
Stock A			
0.7481	2	0.0517	2.31
0.8318	4	0.0524	2.09
0.7738	6	0.0475	1.90
0.8495	8	0.0478	1.88
0.8416	10	0.0351	1.39
0.8973	12	0.0296	1.10
Stock B			
2.0214	0	0.1881	2.36
1.8519	2	0.1381	1.89
1.8627	4	0.1142	1.55
1.8431	7	0.0673	0.93
1.7648	8	0.0594	0.85
		The stock had set up at this point	
Stock C			
0.6572	0	0.0774	2.61
1.0482	2	0.0371	0.79
1.0782	4	0.0196	0.40
1.1756	6	0.0168	0.32
1.2266	8	0.0120	0.22
1.2475	10	0.0256	0.46
1.3438	12	0.0290	0.48
0.9773	14	0.0147	0.33
0.9768	16	0.0212	0.48
Stock D			
1.1893	0	0.0000	0.0
1.2551	2	0.0111	0.185
1.1532	4	0.1120	2.028
1.0745	6	0.1089	2.115
1.0225	8	0.0612	0.7615
1.0225	10	0.0573	0.738
Stock E			
0.6273	0	0.0000	0.0
0.7702	1	0.0622	2.17
0.7812	2	0.0983	3.11
0.9658	3	0.1486	3.89
0.8470	4	0.1336	3.97
0.8131	5	0.0382	1.19
0.9051	6	0.0227	0.63
0.7177	8	0.0021	0.074
Stock F			
0.9357	0	0.0066	0.179
0.7930	1	0.0035	0.114
0.9464	2	0.0006	0.016
0.9537	3	0.0164	0.440
0.8525	4	0.0405	1.210
0.8725	6	0.0336	0.980
1.0550	8	0.0224	0.514
Stock G			
1.0584	0	0.0070	0.119
0.9235	2	0.0480	1.330
0.9853	4	0.0293	1.754
0.9601	6	0.0041	0.109
0.9031	8	0.0010	0.028

small pieces and placed in a beaker containing 200 cc. of benzene. The beaker was placed under a stirrer and its contents stirred for 6 hours, by which time the rubber had become thoroughly dispersed in the benzene. The contents of the beaker was transferred to a separating funnel and the solution thoroughly extracted four times with a 10 per cent solution of sodium carbonate in water. The uncombined sulfur passed into the carbonate solution. The benzene solution was washed with 100 cc. of distilled water to remove the last traces of carbonate, the washings being added to the carbonate solution. The solution was then brominated and acidified. It was boiled to remove excess bromine and all traces of carbonate, leaving the extracted sulfur in the form of sodium sulfate. The sulfate was estimated in the usual way by precipitation as barium sulfate.

The results are given in Table 10.

With the sulfur-accelerator mixings, the curves (A, B, and C) follow along the lines expected, the stock having the greatest velocity of reaction with sulfur being also the stock which would not bond to brass. The superaccelerated mixes (curves D, E, F and G) appear to be characterized by a large release of sulfur in the initial stages.

The above results have been graphed in Figure 5.

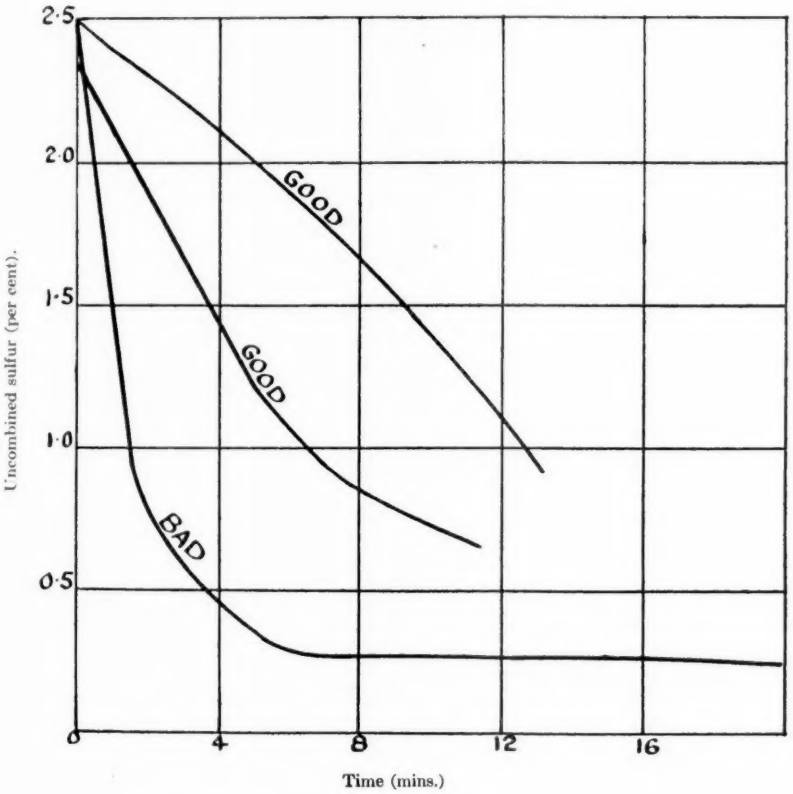


FIG. 5.—Sulfur-accelerator.

That this takes in the case of the Vulcaplas and Novoplas is easily understandable, since both these are known to decompose, with release of sulfur, at curing temperatures. It is not quite so clear, however, why such a large release is obtained with the tetraethylthiuram disulfide mixing. There is substantial evidence that the zinc in the rubber combines well with tetraethylthiuram disulfide to form the zinc complex[9]. Since this complex is soluble in weak alkali, it would be extracted by sodium carbonate solution, probably as sodium diethydithiocarbonate. The action of bromine would convert most, if not all, of this complex to sodium sulfate. Experiments to prove this indicated that 33 per cent of the zinc complex is finally realized as barium sulfate. There is also the possibility that a portion of the tetraethlythiuram disulfide is decomposed, with release of free nascent sulfur instead of

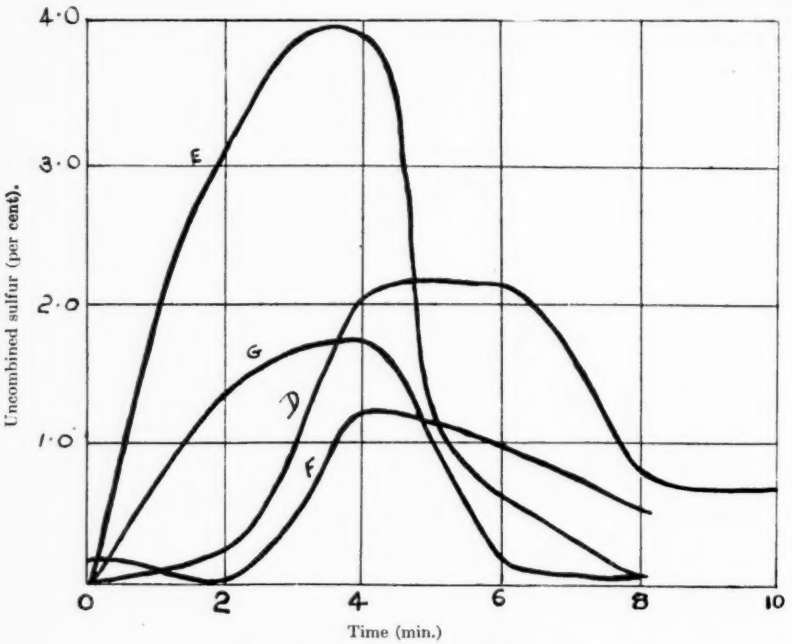


FIG. 6.—Rate of reaction of rubber with sulfur.

changing over completely to the zinc complex, as previous investigators have postulated. These two factors operating jointly can account for this apparently large release of sulfur followed by rapid setting-up of the rubber.

Lastly, Figure 6 illustrates the effect of the sulfur content of a rubber mixing on its bonding properties. The percentage of rejects (all parts showing bare brass were counted as rejects) were plotted against the percentage composition of the brass. Curve 1 is that given by Stock A and contains 2.5 per cent of sulfur. Curve 2 is that of a stock similar to A, but having 5 per cent of sulfur. It can be seen that Stock A has by far the better bonding properties. Two peaks of good adhesion are also in evidence and occur at the same composition for each stock, the first at about 70 per cent, the second at about 80 per cent of copper. This is probably due to the physical condition of the brass, *e.g.*, uniformity of deposit, orientation, etc.

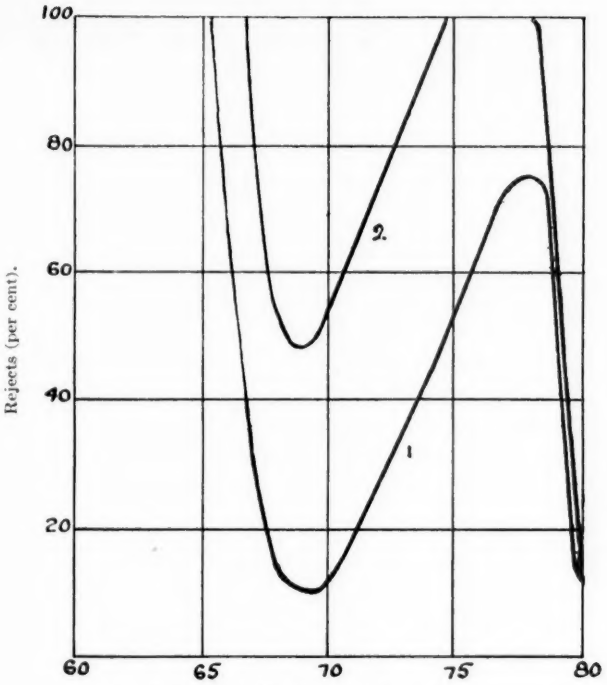


FIG. 7.—Effect of increasing the amount of sulfur.

SUMMARY

In the initial stages of the reaction at the rubber-brass interface, formation of cuprous sulfide takes place. After this compound is formed, three possible reactions can occur.

(1) The cuprous sulfide can unite with a "free" sulfur atom to form cupric sulfide.

(2) The cuprous sulfide can attach itself to a sulfur atom already combined with the rubber.

(3) The cuprous sulfide can attach itself directly to the rubber at points of unsaturation.

In all cases of bad bonding brass examined by physical means, failure appeared to be due to nonuniformity in the structure of the plating. This lack of uniformity gave rise to a greater degree of corrosion and to conversion of the cuprous sulfide formed in the first place to cupric sulfide.

Secondly, bad bonding stocks were characterized by two things:

(1) The rate of reaction of the sulfur with rubber proceeded at a greater pace.

(2) A greater degree of sulfide formation occurred at the brass rubber interface.

This implied that reaction (2) was taking place, with the added complication of chains of sulfur atoms between rubber and copper.

In other words it is necessary that a proper balance be maintained between the velocities of combination of sulfur with rubber and with brass. Thus, when the balance is disturbed, for example, by addition of more active accelerators, or, if the brass is in a more reactive state, then failure in adhesion results.

Conclusion.—From experiments carried out it would appear that bond development occurs through formation, first of cuprous sulfide, which then reacts with the rubber molecule attaching itself to it at points of unsaturation.

References have appeared from time to time in the literature to the effects of copper on rubber, and it is suggested that copper acts as a catalyst for the depolymerization of rubber in its immediate vicinity, thereby providing reaction linkages for the attachment of cuprous sulfide.

ACKNOWLEDGMENT

Acknowledgment is made to the Andre Rubber Company for permission to publish this paper.

REFERENCES

[1] Buchan and Shanks, *Trans. Inst. Rubber Ind.* **21**, 266 (1945); preceding paper in this issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[2] Ferguson and Sturdevant, *Trans. Am. Electrochem. Soc.* **38**, 166 (1920).
[3] McCortney, *Vanderbilt News*, Dec. **1933**.
[4] Buchan, *Trans. Inst. Rubber Ind.* **19**, 25 (1943).
[5] Satake, *J. Rubber Ind. Japan* **8**, 461 (1935).
[6] Fischbeck and Dorner, *Z. anorg. Chem.* **182**, 282 (1929).
[7] Fischbeck and Dorner, *Z. anorg. Chem.* **184**, 167 (1929).
[8] Buchan and Rae, *Trans. Inst. Rubber Ind.* **20**, 205 (1945).
[9] Clarc, LeTourneau and Ball, *Ind. Eng. Chem.* **35**, 198 (1943); Dufraisse and Jarrijon, *Compt. rend.* **215**, 181 (1942).

THE MOBILITY OF FOREIGN MOLECULES DISSOLVED IN RUBBER *

JEAN HAEGEL

INSTITUTE OF CHEMISTRY AND PHYSICS, UNIVERSITY OF BÂLE, SWITZERLAND

INTRODUCTION

Current theories of the elasticity of rubber view this property as originating in thermal agitation of the rubber molecules themselves. In any consideration of this problem, a major point to be considered is the degree of freedom of this agitation, first, because only segments of these very long molecules are concerned, and secondly because large brownian movements which might otherwise profoundly alter the structure are impossible. These phenomena should hold true also of rubber containing no solvent to swell it.

A convenient means of studying thermal agitation of this character is to investigate the mobility of foreign molecules or segments of these molecules when they are dissolved in rubber. This can be done in a practical way by adding a colored substance to the rubber.

Investigations already carried out in the laboratory have not completely settled this problem, but at least have led to rather unexpected results; it therefore seemed advisable to continue the study.

PREVIOUS INVESTIGATIONS

Experiments carried out by Suhr[2] seem to prove that foreign molecules diffuse in rubber. The part of his work which is of particular concern in the present problem involves three series of experiments: (1) diffusion in vulcanized rubber swollen by benzene, (2) diffusion in vulcanized rubber in its normal state without any solvent present, and, finally (3) experiments, the purpose of which was to prove that orientation of a dye takes place after rapid elongation of rubber. In this last case the dichroism which, under these conditions, appears in a film of colored rubber served as an indication of such orientation. The substances which were tested included carotene (mol. wt. 536), *p,p'*-azophenol distearate (mol. wt. 746), and four dyes with very long molecules and molecular weights ranging from 1086 to 1250. Suhr proved that, in rubber swollen by benzene, it required several minutes for a film 1–2 mm. thick, containing carotene to become uniformly colored, one hour with azophenol distearate, and 25–30 hours with the two dyes with high molecular weights. In rubber containing no solvent, the author found no evidence of diffusion of any of the four coloring agents, even after months. Unfortunately he did not mention whether, in these prolonged tests, the rubber films were protected from oxidation, because to color them they were immersed in benzene, which extracts the antioxidants ordinarily added to rubber. In a third series of tests, the films were mounted in an apparatus where they could be stretched rapidly. By means of an optical device it was possible to detect any dichroism

* Reprinted from *Helvetica Chimica Acta*, Vol. 27, No. 7, pages 1669–1684, December 1, 1944.

which might appear at the moment when the maximum point of stretching was reached. Carotene was used as the coloring agent. No effect of this kind was found by the author. The time, as measured by the present author, required in the apparatus of Suhr to stretch a film of rubber to 100 per cent elongation was approximately 0.007 second, *i.e.*, greater than that estimated by Suhr. In view of this it becomes necessary to reëxamine his conclusions.

Kuhn, Suhr and Ryffel[3] have completed the work of Suhr described above, and have observed the following facts. In vulcanized rubber swollen by benzene, an increase from 500 to 1200 in molecular weight of the dissolved substance lowered the diffusion constant by a factor of 200 instead of the factor 1.5 which was expected. The diffusion constant of phenol in rubber which was not swollen was found to be 10^{-11}, but an error was found later, and the true value of 10^{-8} was published in a later work[4]. The experiments, which give indications of an orientation of the coloring agent when the rubber film was stretched rapidly, were repeated with the same apparatus and with a coloring agent having a molecular weight of 1250 (the same as that used in the present work, as will be described later). Under these conditions the authors were able to prove that there was a permanent orientation of the coloring agent in the stretched rubber. This effect should have given a diffusion constant equal practically to zero and should have confirmed, by means of a more sensitive method, the data already published by Suhr and confirmed in the later publication on the diffusion of these coloring agents of high molecular weight in unswollen rubber. Nevertheless these authors believed it advisable to be cautious in drawing conclusions.

Meantime experiments now being carried on by F. Grün in the same laboratory indicate that the diffusion constant of this coloring agent in vulcanized rubber is far from infinitely small, as a result of which he has been led to believe that the permanent orientation must be explained in some other way. It was, therefore, of interest to undertake a detailed investigation of the subject.

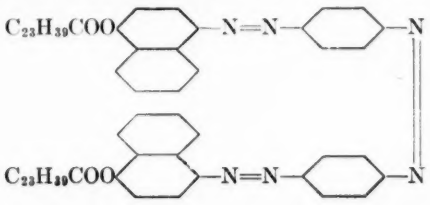
It follows from all this that the diffusion of foreign molecules dissolved in rubber takes place under very abnormal conditions and that the simple laws governing the relations between the molecular weight of the dissolved substance, the viscosity of the solvent, and the diffusion constant are not applicable as such to the phenomena which take place when substances are dissolved in rubber. Within a certain range of molecular weights, the diffusion constant decreases far more rapidly than for an ordinary liquid.

THE PRESENT INVESTIGATION

The chief purpose of the present work has been to extend, by means of a more highly developed apparatus, the work already carried out by Suhr[2] and by Kuhn, Suhr and Ryffel[3], with a view to detecting any orientation of the long molecules of a coloring agent which may be brought about by the rapid elongation of a film of rubber in which the coloring agent is dissolved by taking advantage of the dichroism exhibited by the oriented coloring agent. Such experiments are of interest because, as has already been pointed out in the discussion above, the diffusion in rubber of substances having high molecular weights is quite abnormal in relation to the behavior of substances of low molecular weight when the diffusion constants are measured in the conventional way, *i.e.*, by analyzing the free diffusion through a distance of at least 0.1 mm. It was of interest to know whether this anomaly is still true of distances of the order of magnitude of molecular dimensions themselves.

To answer this question, consider a film of rubber colored by a substance with long chain molecules. Suppose that, by means of some suitable device, it is instantaneously stretched to several times its initial length. The molecules of coloring agent will be in part oriented parallel to the direction of elongation, and optical examination will show dichroism of the rubber film. However, this dichroism tends to disappear because of diffusion of the molecules of coloring agent, in which case it follows a decreasing exponential function, and it may be assumed that, as a first approximation, the time of relaxation of this phenomenon is equal to the time required for the molecules to diffuse through a distance equal to half their length. In this way it is possible to estimate the diffusion constant through a distance of a considerable fraction of an Ångstrom unit. Since long flexible molecules are concerned, this amounts, in short, to measuring the time required for the microdiffusion of different segments of the molecule to lose the orientation which is present in the beginning.

The negative results obtained in the experiments carried out by Suhr can be explained by the relatively rapid diffusion of the carotene and an underestimation of the time required to stretch the rubber samples in the apparatus. The experiments were repeated by the present author with an improved form of apparatus and coloring the rubber film with an agent having very long chain molecules, of molecular weight 1250, already used by Suhr[2] in his measurements of diffusion and by Kuhn, Suhr and Ryffel[3] in their experiments on orientation.



The $C_{23}H_{39}CO$ group is a mixture of 9- and 10-phenylstearic acid residues. The total length of this molecule is estimated to be approximately 80 Å.U. Its diffusion constant for long distances is approximately 10^{-11} to 10^{-12} (according to measurements of F. Grün not yet published).

If the same constant is valid for diffusion through very short distances, the time of relaxation of the dichroism should be:

$$\lambda = \frac{x^2}{2D}$$

$$\frac{(40 \times 10^{-8})^2}{2 \times 10^{-12}} > \lambda > \frac{(40 \times 10^{-8})}{2 \times 10^{-11}}$$

$$10^{-1} \text{ sec.} > \lambda > 10^{-2} \text{ sec.}$$

where λ is the time of relaxation, x is the distance of diffusion, and D is the diffusion constant.

As has been mentioned, Kuhn, Suhr and Ryffel[3] proved the existence of permanent dichroism with this coloring agent. This induced the present author to make a more extended study of the optical phenomena which appear when colored rubber is stretched, so as to eliminate as far as possible what, in all probability, is a parasitic phenomenon before undertaking the major part of the work.

STUDY OF THE PERMANENT DICHROISM BROUGHT ABOUT BY STRETCHING COLORED AND UNCOLORED RUBBER

As early as 1874 Kundt[5] observed that highly stretched rubber is dichroitic. This phenomenon is very easily observed with whatever apparatus happens to be available. To study the phenomenon spectrographically, a film of rubber was stretched and placed between two glass plates, with interposition of a suitable immersion liquid[6] because of the roughness of the surface which is always encountered under such conditions. Through the film of rubber made transparent in this way, and placed at the eyepiece of an optical system, is projected the image of a Rochon double prism on the slit of a spectrograph, composed of two halves side by side, polarizing the light so that they are parallel and perpendicular, respectively, to the direction of stretching of the rubber. The source of light was an iron arc. In the absence of rubber, this image was a small luminous rectangle, composed of two equally illuminated halves and corresponding to the two halves of the prism. When a dichroitic object was placed in the path of the light, the luminous intensity was different in the two halves of the image.

When the stretched rubber film[7] was in place, the image of the Rochon prism took on the appearance shown in Figure 1. The part corresponding to the ray whose electric vector was perpendicular to the direction of stretching is very distinct. On the contrary the ray parallel to the direction of stretching is very much weaker; it is strongly diffused, but only in the plane perpendicular to the direction of stretching[8]. This obviously precludes the possibility that rubber itself shows any true dichroism, for the quantity of light polarized parallel to the direction of stretching and lost by diffusion is not known (Scherrer-Toss[9] suspected the part played by diffusion in the dichroism of rubber).

By means of an oscillating mirror, the image shown in Figure 1 was displaced from left to right and from right to left on the slit of the spectrograph in such a way as to integrate automatically the diffused light. In this way the presence of a true dichroism was proved, extending throughout the visible and near-ultraviolet absorption band of the clear yellow rubber used. The ray polarized parallel to the direction of stretching was weaker than that polarized perpendicularly. Figure 2 is identical with Figure 1 except that in Figure 2 the diffused light is integrated. In this way the true dichroism of the stretched rubber is made evident. Naturally there is still the possibility of a rather large loss by diffusion in the direction in which the light enters.

The great irregularity of this phenomenon of double diffusion (or dityndallism), which in some cases was very intense, in other cases hardly visible or nonexistent, was very puzzling, and this made it all the more interesting to find out what optical heterogeneity was responsible for such a diffusion of light.

From the optical point of view, this phenomenon can be explained satisfactorily if it is assumed that the particles which are responsible for it are elongated and oriented parallel to the direction of stretching, and that their transverse dimensions are of the same order of magnitude as the wave length of the light used, or at most only a little greater.

Actually, with a suspension of spherical particles which are small compared to the wave length of the incident light, the Tyndall effect is at its maximum in the direction which is at the same time perpendicular to the direction of the incident pencil of light and to the plane of polarization of this pencil. If the particles are elongated and oriented in parallel, only the ray which is polarized parallel to the direction of orientation of the particles gives a Tyndall

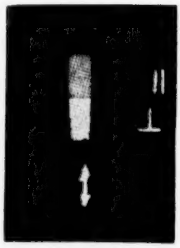


Fig. 1.

Fig. 2.

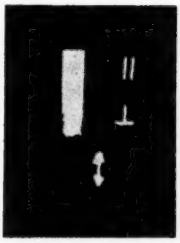


Fig. 3.

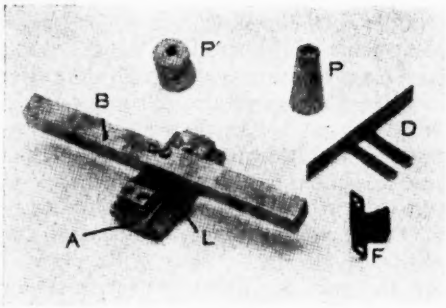


Fig. 4.

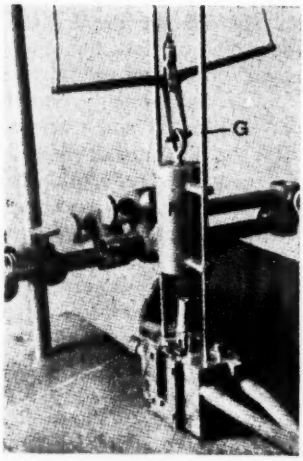


Fig. 6.

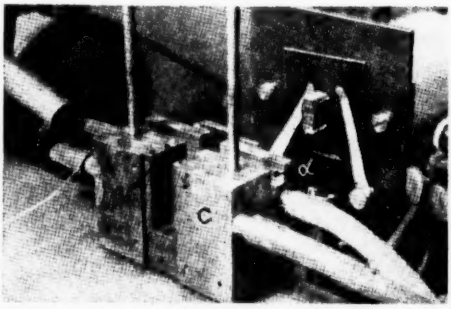


Fig. 5.

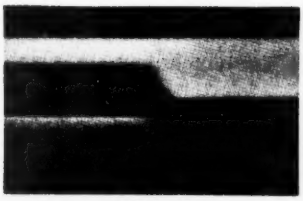


Fig. 7.

FIG. 1.—Double diffusion of light in rubber stretched to 300 per cent elongation. The double-pointed arrow indicates the direction of stretching.

FIG. 2.—Dichroism of stretched rubber (300 per cent elongation). Integration of diffused light.

FIG. 3.—Rubber stretched to 300 per cent does not exhibit at 60° C any dichroism or any double diffusion.

FIG. 4.—Apparatus for stretching rubber samples; taken apart to show internal parts.

FIG. 5.—Apparatus for stretching rubber samples; the receptacle.

FIG. 6.—Apparatus for stretching rubber samples. Assembled.

FIG. 7.—Displacement of the movable part of the apparatus for stretching as a function of the time. The abscissa represents the time (from left to right 7 mm. = 0.001 second). The ordinate represents the displacement (natural size).

effect. If the particles are large in relation to the wave length of the light employed, the maximum is displaced toward the direction of exit of the incident ray. This is just what Figure 1 shows. The aperture angle of the diffused rays is approximately 10°.

It should be mentioned that the utilization of this phenomenon in a quantitative way, with the aid of the theory of Rayleigh, as extended by Miè, Möglich, Blumer, etc., with a view to drawing conclusions concerning the form of particles and their size, is very uncertain if not impossible. As a matter of fact not only do the phenomena become very complex when the particles are of this order of magnitude, but even if the indices of refraction of rubber in the two principal directions are known, the indices of refraction of the particles responsible for the diffusion are unknown.

The question still remains as to the nature of these particles and whether they may not be impurities in the rubber. One striking fact is the irregular appearance of the phenomenon. Some films of rubber show it easily at low elongations; others seem to give no such manifestation even at high elongations. It should be particularly noted that after a sufficiently long time, *e.g.*, eight days, all films of rubber showed the phenomenon. The effect increased greatly as the temperature decreased toward 0° C, and it disappeared completely at a temperature range of 30° to 70° C, in this latter case the actual temperature being higher the greater the percentage elongation and the longer the time that the rubber was stretched. Above this critical temperature no dityndallism or dichroism was observed (see Figure 3).

All this immediately suggests that the particles which are responsible are none other than crystallites of rubber, which, moreover, at any given degree of elongation, are much more highly oriented than the molecules themselves. It is known, for example, that the melting point of crystallites increases with the degree of elongation and with the time[10]. Furthermore it is known that, for the same percentage elongations at which the effect has been observed, the double refraction increases with time, an indication of crystallization[11]. The irregularities in the appearance would, therefore, be explainable by the presence or the absence of crystalline germs. Rubber which has been stored for a long time gave a very rapid effect (30 seconds), which was very distinct at an elongation of 150 per cent, whereas when the rubber was previously heated at 40–50° C or was swollen in benzene to cut the films on a cold-temperature microtome, which melts the germs, it was frequently necessary to wait several days. In this case the phenomenon was one of superfusion. Furthermore, even without any apparatus, it may be readily observed that the crystallization of rubber, whether stretched or not stretched (in this case unvulcanized rubber), is manifest by the rubber becoming opaque, and by this opacity disappearing again when the crystalline state is destroyed by heating or by mechanical deformation.

But even in the most unfavorable cases, at ordinary temperatures, this phenomenon requires several seconds to take place, and does not interfere with observations made during the first fractions of a second following instantaneous elongation.

The films of rubber used in the experiments described above were 2–3 mm. thick before being stretched. When a film only 0.1–0.2 mm. thick is stretched, these effects are too weak to be visible. But suppose that this film of rubber is colored[12] by means of some suitable coloring agent, having very long chains, such as that described earlier and the constitution of which has been given. If this colored film is stretched, it will be found that after a length of time approximating that necessary for untreated rubber to crystallize, a strong

dichroism becomes evident, attributable obviously to the coloring agent, since the film of rubber is so thin. This dichroism has no connection with any orientation of the molecules of the coloring agent resulting from stretching of the rubber; in fact it appears only sometime after the stretching operation is finished, and when the natural diffusion of the coloring agent should long since have broken up any such orientation. Furthermore it increases with time. This suggests that the effect is connected with the effects discussed above, which depend on crystallization of the rubber. It is still more evident when a film of rubber which is stretched and shows dichroism is heated. In this case the dichroism disappears at the same temperature at which crystallization disappears. On the contrary, when the stretched sample is cooled, its dichroism increases greatly. Circumstances have prevented the present author from carrying out tests with other substances, but it may be easily demonstrated that the effect described depends to a considerable extent on the particular coloring agent used.

The simplest hypothesis which can be advanced is to assume that the crystallites which form in the rubber adsorb or dissolve the long-chain coloring agent, at the same time orienting it in some preferential direction with respect to the crystallites. But the crystallites themselves are highly oriented in a stretched film of rubber, and the coloring agent itself also becomes oriented, so that it no longer adsorbs in the same way polarized light parallel or perpendicular to the direction of its chromophore groups.

From the intensity of the blackening of the photographic plate by polarized rays parallel or perpendicular to the direction of stretching, it is possible, if it is assumed that the coloring agent is completely dichroitic, to calculate the proportion of the coloring agent which is oriented. The weakening of the luminous pencils is approximately 1000-fold after passage in the film of rubber. The relation between the two blackening effects for an elongation of 200 per cent is around $\frac{1}{2}$ to $\frac{1}{4}$. Under these conditions it follows that 10 to 20 per cent of the coloring agent is oriented by the crystallites. This is likewise the maximum proportion of rubber crystallized under the same conditions, provided it is assumed that the oriented coloring agent is at the exact location where crystallization takes place. However, it is evident that the molecules can migrate by diffusion and thereby reach a crystallite; hence any exact estimation of the phenomenon is out of the question.

It may be remarked in passing that this explanation of the dichroism of stretched colored rubber applies as well to the dichroism of natural rubber, for if the latter is purified it no longer shows any absorption band in the visible spectrum; accordingly its dichroism must be due to the presence of foreign coloring substances, which give it its yellow color.

The effects which have just been discussed do not offer any obstacle to the measurement of the dichroism of colored rubber provided the measurement is made immediately after stretching, for with such rapid measurements, there is no time for crystallization to intervene.

INVESTIGATION OF A TEMPORARY DICHROISM CAUSED BY THE RAPID STRETCHING OF COLORED RUBBER

THE APPARATUS

In this investigation an apparatus was used which had been developed for a different purpose where it was important that samples not only be elongated very rapidly but at the same time linearly. It was not possible to use, as did

Suhr[2], a suddenly released spring to stretch the rubber samples, for the elongation would then follow a parabolic course.

The apparatus is made up of three essential parts, a movable part A, a fixed clamp B, and receptacle C. The rubber film is visible at L in Figure 4, mounted between the fixed clamp B and the movable part A. Figure 4 shows the movable part resting on the table, and the fixed clamp placed on the movable part in the respective positions which these two pieces have when the apparatus is assembled. The rubber sample is fixed on B by a clamp similar to that seen at A, placed on the invisible face of B, and fastened by two screws which can be seen in the photograph.

The receptacle C (see in Figure 5) has on its upper part a channel α, into which the fixed clamp is inserted, and can be fastened in place by two screws with polished heads. The movable part A slides in two vertical channels β located opposite each other on the interior walls of the receptacle. When the movable part A is at the top of its stroke, the rubber sample is at rest. When the movable part is made to slide downwards, the rubber sample is stretched. The optical observation is made through a slot in the movable part A, the top of which is just visible above the fixed part B.

Figure 6 shows the assembled apparatus. In front and on top a brake is visible (F in Figure 4), which is attached to the front face of the movable part A.

The force necessary to stretch the rubber sample is supplied by the hammer M, which slides on the guides G. The total height of these guides is 6 meters, and in its free fall the hammer reaches the bottom at a velocity of 10 meters per second, at which velocity it strikes the movable part and penetrates it immediately to end the fall. A lead plug, whose shape has been determined by trial, is placed on the movable part for the purpose of transmitting the force of the hammer, and then absorbing the excess energy by crushing when the film of rubber is stretched and A touches the bottom of the receptacle C. Its final shape is shown as P′ in Figure 4.

By proper adjustment of the braking action and of the lead plug, it is possible to stop the stretching completely without any tendency to rebound on the base of the receptacle, which is placed on an ordinary blacksmith anvil, so as to give stability to the assembly.

D is a diaphragm which stops any stray radiation, and which can be placed inside of the receptacle C. The latter can be closed by two window panes, a feature which makes possible a closer control of the temperature, which is regulated by circulation of air (containing alcohol for temperatures below zero) from a thermostat.

When the apparatus is assembled and mounted, with the unstretched film of rubber in place and the hammer M at the top, a pull of the cord attached to the arms of the clasp on which the hammer is suspended frees the latter so that it falls approximately 30 cm. and thereby operates a small level which opens a photographic shutter, stretches the rubber, and crushes the lead plug.

The rubber film, which originally is 3 mm. long, is stretched to 12 mm. The hammer weighs 350 grams, and when it strikes the rubber at the bottom of its fall, it is travelling at a velocity of 10 meters per second. The assembly of movable parts weighs 35 grams, and is, therefore, impelled almost instaneously with a velocity of 9 meters per second. The break in the fall, which takes place without rebound on the steel base of the receptacle, is likewise practically instantaneous. Figure 7 shows a photographic recording of the displacement of the movable clamp. The elongation is practically linear to 300 per cent and requires 0.001 second, *i.e.*, with a linear velocity 21 times as great as in the

apparatus used by Suhr[2]. Both calculations and experiments show that friction, due principally to the brake, is negligible compared with the kinetic energy of the hammer.

OPTICAL APPARATUS

The optical device is mounted on two optical frames placed on both sides of the stretching receptacle. The front part acts as a condenser C (Figure 8), which projects the image of an arc lamp S on the rubber sample. A filter F, 5 cm. thick, and filled with copper sulfate solution, is placed in the path of the light, so as to prevent heating of the sample during its short time of illumination, and to absorb the major part of the radiation outside of the absorption region of the color used, which has a single very broad band from 500 to 300 mμ and almost constant depth ($\log \epsilon = 4.5$)[2]. The rubber film serves, therefore, as a secondary source of light, and it is the light from this source that the back part of the optical assembly analyzes.

The aperture of the front part has been purposely chosen very large (f 1.5), while the material available has made it necessary to use a very small aperture

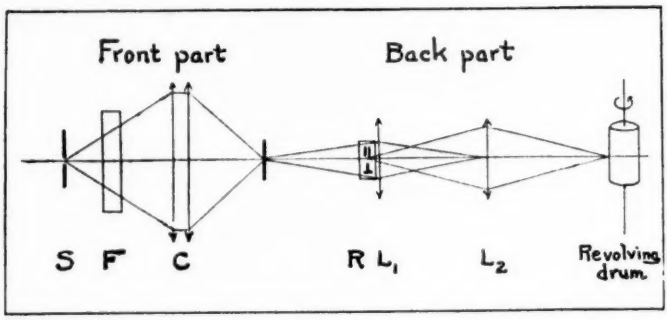


FIG. 8.—Schematic diagram of the optical apparatus. The diaphragms, screens, and shutters are omitted.

(f 30) in the back part of the optical assembly. This combination, which is equivalent to the reverse combination (a very narrow pencil and wide aperture in the back part), avoids the use of an immersion liquid, which would be a source of difficulty because of the enormous acceleration of the moving parts.

The back part, consisting essentially of a Rochon prism R made up of two superposed halves, gives two polarized rays, one parallel, the other perpendicular to the direction of stretching of the rubber. A lens L_2, placed against the prism, projects to the opening L_2 the image of the rubber film, which is the source of light. L_2 is a photographic objective equipped with a shutter released by the fall of the hammer. It projects the image of R on the drum carrying sensitive film. This image is a small luminous rectangle, divided into two halves, one of which is polarized parallel to, the other perpendicular to, the direction of elongation of the rubber. The drum carrying the sensitive film turns in such a way that these two parts record on the film two tracks of equal intensity as long as the rubber sample does not exhibit any dichroism. Control tests make it possible to check the adjustment of the apparatus.

The rotating drum is driven by an adjustable-speed motor, and is connected permanently with a tachometer, and the speed is such that 0.001 second is

recorded as a distance of 1 cm. The image of the Rochon prism on the film has a width of 1 mm., so it is possible to estimate the variations in relative intensity of one region with respect to another for a time interval of the order of 10^{-4} second. The calculation already carried out (*loc. cit.*) shows that with this apparatus it is possible to estimate a diffusion constant of the coloring agent less than 10^{-9}.

RESULTS

Under the experimental conditions which have just been described, it was impossible to obtain any evidence of the slightest temporary dichroism due to orientation of the coloring agent brought about by stretching the rubber, even when the rubber sample was chilled to $-5°$ C, a procedure which would be expected to decrease the diffusion constant of the coloring agent in the rubber. Although for a range of several tenths of a mm. this coloring agent had in rubber a diffusion constant of the order of 10^{-11} to 10^{-12}, microdiffusion through a range of about 40 Å.U. took place with a diffusion constant certainly greater than 10^{-9} sq. cm. per second.

CONSEQUENCES

If we confine ourselves to diffusion in vulcanized rubber free of solvents, it will be evident that if the macrodiffusion of a large molecule is very abnormal in comparison with that, for example, of phenol, the microdiffusion of this same molecule approaches orders of magnitude several times that of the normal value. Use can be made of the formula of Einstein and Smoluchowski to describe these phenomena. This formula gives the diffusion constant D of a molecule of radius r in a liquid of viscosity as follows:

$$D = kT \frac{1}{6\pi\eta r}$$

where k is the Boltzmann constant and T is the absolute temperature. Extrapolation is obviously necessary, since this formula, established on the basis of hydrodynamic considerations, is strictly valid only for colloidal suspensions of spherical particles[13]. However, it can easily be proved that the formula gives a quite acceptable order of magnitude for molecular solutions, *e.g.*, sucrose in water, if it is granted that there is a certain degree of arbitrariness in assigning a value to r for a nonspherical molecule. But since in any case it is necessary to limit the calculation only to orders of magnitude, the use of this formula seems to be justified.

With the relation of Einstein and Smoluchowski, it is possible to explain the anomalies in diffusion which have been described in the experimental part of the present work as anomalies in the viscosity of the solvent (rubber) with certain molecules and under certain conditions. It might seem unjustifiable to extrapolate the concept of viscosity to such a point, the usual definition of which is purely mechanical and macroscopic, in order to define the diffusion of simple molecules, particularly when the viscosities concerned are out of macroscopic range. However, such an extrapolation has been carried out because the macroscopic viscosity of an ordinary liquid makes it possible to define the conditions of diffusion, and because the factor which is introduced by this term, even if not evident macroscopically, will always have the magnitude of a viscosity.

According to this concept and in accordance with the relation of Einstein and Smoluchowski, rubber does not show the same viscosity with respect to a molecule of phenol that it does to a molecule having a molecular weight of about 1000, nor with respect to macro- and microdisplacements of this molecule.

Furthermore the viscosity is not the same in the range necessary for diffusion of phenol as it is for the diffusion of large molecules. By the term range required for the diffusion of a given molecule is meant the volume encompassed by an elementary displacement of this molecule, and since in any case it is a question of order of magnitude and since it is not desirable to carry the analysis too far, it may simply be said that a molecule whose linear dimensions are xÅ requires for its macrodiffusion a range of the linear order of magnitude of xÅ.

On the basis of the definitions which have just been proposed, it is possible to lay down the following proposition, which embodies the experimental results of this work and of previous investigations, *viz.*, that *the viscosity of rubber varies according to the range under consideration.*

We shall now attempt to see whether prevailing theories of the elasticity of rubber are in harmony with this proposition.

A piece of vulcanized rubber of ordinary dimensions has an infinite viscosity since, when it is deformed, the forces which result from this deformation do not disappear. Consequently the rubber does not flow. On the other hand, the concept of freedom of micromovement of the molecules which compose it, a phenomenon which is the basis of kinetic theories of the elasticity of rubber, rests on the assumption that the viscosity within a very small range is slight or at least measurable. It is this concept which it is attempted in the present paper to explain on a quantitative basis.

As is known, the properties of a real rubber can be defined only by taking into account several elastic mechanisms, which differ (1) in their partial moduli of elasticity contributing to the integral modulus of elasticity of the rubber after sudden elongation, and (2) by their times of relaxation[14].

It is now generally agreed that these times of relaxation are not characterized by discrete values, but are, rather, scattered through several more or less extended zones, or even form a continuous series extending from infinity to extremely small values.

As far as the present problem is concerned however, it is sufficient to group these mechanisms in four categories.

(α) Modulus of elasticity $E_\alpha = 10^6 - 10^7$; time of relaxation $\lambda_\alpha = \infty$. This is the most important mechanism of vulcanized rubber. In virtue of this, when a sample of rubber is deformed, the resulting forces which are set up do not disappear. Consider then the kinetic theory of elasticity of rubber. This elasticity depends on the freedom of the segments of a molecule located between two fixed points. The time of relaxation is related to the mean life of these fixed points. The modulus of elasticity is determined by the molecular weight of the free segments.

A relation derived by Kuhn[15] makes it possible to calculate this molecular weight M when the modulus of elasticity E and the density δ of the elastic high polymer under investigation are known:

$$M = 7RT(\delta/E)$$

where R is the constant of perfect gases and T is the absolute temperature. This relation obviously assumes that all molecules of the substance under investigation participate to an equal extent in the mechanism under consideration. With the aid of this relation, M values of the order of 20,000 to 200,000

for ordinary vulcanized rubber are obtained. According to what is known about the constitution of rubber[16], these molecular weights correspond to mean free lengths of 1000 to 10,000 Å.U.

The mean distance h between the two extremities of a chain of this length has been calculated by Kuhn[17]. If A is the length of the statistical element of the chain, and N is the number of elements in the length of chain under consideration, then $h = A\sqrt{N}$. If A is assumed to be 20 Å.U., then N is 50 to 500, and 140 Å.U. $< h <$ 440 Å.U.

It is evident that a molecule whose order of magnitude is greater than these dimensions cannot pass through meshes of this size. Compared to it, rubber would have an infinite viscosity. On the contrary a molecule of phenol, for example, can diffuse into the interior of such a network practically as if it did not exist. For it the viscosity of rubber would be low.

(β) $E_{\beta_0} = 10^2$ to 10^6; $\lambda_\beta = 10$ to 10^4 seconds. These mechanisms[18] are responsible for the plasticity of rubber, which is in general a fault even in its technological applications because of the relatively high value of λ. The partial modulus E_{β_0} is, in the case of vulcanized rubbers, lower than E_α. It is, so to speak, a residual effect from the unvulcanized state of rubber, since vulcanization superposes on the β system (which is preponderant in unvulcanized rubber) a system of bridges of sulfur, thereby creating the α system, which becomes the predominant system.

Since E_{β_0} moduli are smaller than E_α moduli, these mechanisms do not change in any way the conditions of diffusion of foreign molecules, which are determined by the α systems. From the values of E_{β_0} it might, in fact, be concluded either that the free elements of the chain are longer than in the case of α mechanisms, or that only a small part of the molecules participate in the β mechanisms.

The high viscosity found by Van der Wyk[19] in measuring the damping of torsion oscillations of a rubber thread can be attributed to these β mechanisms. A relation derived by Maxwell makes it possible to determine the viscosity of a medium when its torsion modulus G (measured after a sudden deformation) and its time of relaxation λ are known, on the condition that there is a time of relaxation in this medium: $\eta = G_0\lambda$. Or if the modulus of elasticity E_0 is introduced:

$$\eta = 0.5\,\frac{1}{1+\mu}\cdot E_0\lambda$$

where μ is the Poisson coefficient, which is equal to 0.5 for rubber[20]. This relation cannot be applied without modification to a medium where several times of relaxation exist. Kuhn has shown that in this case it is necessary to take the sum of the different partial viscosities, calculated separately for each distinct mechanism:

$$\eta = \Sigma\eta_i = \Sigma G_{i0}\lambda_i = 0.5\,\frac{1}{1+\mu}\,\Sigma E_{i0}\lambda_i$$

The values of E_{β_0} and λ_β are such that the partial viscosity of η_β is of the order of 10^6 poises, a value which corresponds to that measured by Van der Wyk. Now it will be shown that the factor η_β is by far the most important of all the partial viscosities (if $\eta_\alpha = \infty$ is disregarded; in fact in damping measurements, for example, the part played by α mechanisms is solely that of elastic mechanisms). Although incapable of modifying the viscosity of rubber in

small ranges, β mechanisms are responsible for the high viscosity which dampens its macroscopic mechanical oscillations.

(γ) $E_{\gamma_0} = 10^7$ to 10^8; $\lambda_\gamma = 10^{-3}$ to 10^{-4}. This group includes mechanisms to which special study has been devoted in recent years[21], which undergo relatively rapid relaxation, but the partial moduli of which are about ten times as great as E_α. The calculations are the same as for α mechanisms. The length of the free elements of the chain is in the range between 150 and 1500 Å.U., the mean distance between the extremeties, h, is still lower, *i.e.*, about 50 to 150 Å.U.[22]. Ranges of this magnitude are of the order necessary for macrodiffusion of the particular coloring agent used in the experiments, and the partial viscosity η_γ is the primary factor in determining the conditions of diffusion of molecules of this order of magnitude. The relation of Maxwell gives η_γ equal to approximately 10^4 poises.

In the following section it will be shown that it is necessary to assume that this viscosity η_γ is also the only factor which plays an important part in the behavior of these molecules—it is, then, as if the macrodiffusion of the coloring agent took place in a simple liquid having a viscosity η of 10^4 poises. The relation of Einstein and Smoluchowski gives for this molecule and this viscosity a diffusion constant of the order of 10^{-12}, a value in good accord with what has been observed experimentally.

(δ) This group includes all the mechanisms having times of relaxation shorter than 10^{-4} seconds, and for which there are almost no direct experimental data available. Here there must be very high partial moduli as in all substances, even liquids, of the order[23] or 10^{11}, but the times of relaxation are sufficiently short for the viscosity to be of the order of approximately 10 poises.

This value is obtained from the value of 10^{-8} sq. cm. per second of the diffusion constant of small molecules such as those of phenol or of organic solvents within the rubber. On the other hand, it is of the same order of magnitude as the viscosity of high polymeric liquids, in which intermolecular bridges, which account for the elasticity of rubber, are not present.

Likewise it is in the ranges in which the order of magnitude is greater than that of δ mechanisms but less than that of λ mechanisms that microdiffusion of the coloring agent takes place. This is the reason that it has not been possible to obtain evidence of any orientation of the molecules by rapid elongation. It would be interesting to have an apparatus with which it would be possible to stretch a film of rubber 10 to 100 times more rapidly.

According to this concept of the internal state of rubber, a molecule of several hundred Å.U. in solution does not diffuse in the solution at all. A molecule of several multiples of ten Å.U. diffuses as if it were in a medium having a viscosity of approximately 10^4 poises. A molecule of several Å.U. diffuses as if it were in a liquid having a viscosity of 10 poises. This is a consequence of the increasing freedom of brownian micromovement within the rubber.

The present author has found an interesting confirmation of this viewpoint in the way in which the coloring agent diffuses in unvulcanized rubber. Whereas its diffusion constant is 10^{-11} to 10^{-12} sq. cm. per second in vulcanized rubber, it is 10^{-9} to 10^{-10} sq. cm. per second in unvulcanized rubber. This is another indication that, since vulcanization introduces stable intermolecular bonds into rubber, it increases the viscosity in any given range by increasing the moduli of elasticity, and times of relaxation.

It should be pointed out in this connection that the division of the different mechanisms into four distinct groups is purely arbitrary, and has been made

solely with a view to simplification. It is known, in fact, that the combined times of relaxation of rubber form a continuous series which extends from very low values to infinity, a point which has been stressed by Brennschede[24] in particular, and to which Kuhn[2] had previously called attention. In this case the viscosity varies continuously with the magnitude of the range in question instead of decreasing in stepwise fashion as has been described. If the aim had been to make a more exact calculation than was actually done, this simplification would evidently not have been possible, but in this case numerous difficulties would have been encountered, not only because of the lack of experimental data, but also because of the complexity of the phenomena.

RÉSUMÉ

A study of the mobility of foreign molecules dissolved in rubber offers a convenient method for investigating the thermal agitation of small or large magnitude which may be present within the rubber. Current theories of the elasticity of rubber show the importance of this study.

After having eliminated two effects due to crystallization of rubber which would otherwise lead to experimental difficulties, it has been shown, by an optical study of the temporary orientation of a coloring agent of high molecular weight dissolved in a film of rubber which is stretched rapidly, that the diffusion constant of this substance within the rubber depends to a large extent on the distance which the molecule travels in its diffusion. By combining this fact with results already obtained concerning the diffusion of foreign substances dissolved in rubber, the conclusion is reached that the viscosity of rubber must vary according to the range of diffusion under consideration. The relation between this and current theories of the elasticity of rubber are pointed out.

ACKNOWLEDGMENT

The work described in the present paper was carried out in 1943–1944 at the Institute of Physical Chemistry of the University of Bâle. The author wishes to express his appreciation to Professor W. Kuhn for his hospitality, the advice which he has offered so freely, and his continued interest in the work. Thanks are also due F. Grün, with whom the various experimental and theoretical points have been discussed at length, and to whom the present author is indebted for numerous suggestions.

REFERENCES

[1] Wöhlisch, *Verh. physik.-med. Ges. Würzburg* **51**, 53 (1926); Meyer, von Susich and Valko, *Kolloid-Z.* **59** 208 (1932); Kuhn, *Kolloid-Z.* **68**, 2 (1934); *Z. angew. Chem.* **51**, 640 (1938).
[2] Suhr, Thesis, Kiel, **1939**.
[3] Kuhn, Suhr and Ryffel, *Helv. Chim. Acta* **16**, 497 (1941).
[4] Kuhn and Ryffel, *Z. physiol. Chem.* **276**, 160 (1942).
[5] Kundt, *Pogg. Ann.* **151**, 125 (1874); cited by Puffrich, Thesis, Bonn (1881); *Ann. Phys.* **14**, 177 (1881); Scherrer-Tass, *Ann. Phys.* **6**, 278 (1879).
[6] A solution of lithium bromide in glycerol (see Suhr, Thesis, Kiel, **1939**) or of potassium mercuric iodide or potassium cadmium iodide in water of such concentration that the refractive index is 1.52.
[7] The rubber used in all tests was a pure-gum type, lightly vulcanized hot, without any unnecessary ingredients. It was light yellow and practically transparent.
[8] Schwarzenbach (*Helv. Chim. Acta* **12**, 270 (1939) made a similar, through not identical, observation.
[9] Scherrer-Tass, *Ann. Phys.* **6**, 278 (1879).
[10] Von Susich, *Naturwissenschaften* **18**, 915 (1930); Meyer, *Naturwissenschaften*, **26**, 199 (1938); Van Rossem and Lotichius, *Kautschuk* **5**, 2 (1929); cited by Meyer and Mark, in "Hochpolymere Chemie" Leipzig, **1940**, Vol. 2, p. 154.
[11] Thiessen and Wittstadt, *Z. physik. Chem.* **B41**, 33 (1938).
[12] All the colored rubber samples were made by immersing the films in a benzene solution of the coloring agent, in which they swelled, and under which conditions the coloring agent diffused into the rubber rapidly. The benzene was then removed by evaporation in a vacuum at about 150° C (see Suhr, Thesis, Kiel, **1939**).

[13] See the work of J. Perrin.
[14] Kuhn, *Z. physik. chem.* [B] **42**, 1 (1939); *Z. angew. Chem.* **52** 289 (1939); Brennschede, *Kolloid-Z* **104**, 1 (1943).
[15] Kuhn, *Kolloid-Z.* **76**, 258 (1936).
[16] Meyer and Mark, "Hochpolymere Chemie", Leipzig, **1940**, Vol. 2, p. 116.
[17] Kuhn, *Kolloid-Z.* **68**, 2 (1934).
[18] There are numerous technical publications, *e.g.*, Hauk and Neumann, *Naturwissenschaften* **26**, 365 (1938).
[19] Van der Wyk, *Proc. Rubber Tech. Conf. London*, **1938**, p. 985; cited by Meyer and Mark, "Hochpolymere Chemie", Leipzig, **1940**, Vol. 2, p. 156.
[20] Memmler, "Handbuch der Kautschukwissenschaft", Leipzig, **1930**, Vol. 1, p. 439.
[21] Brennschede, *Kolloid-Z.* **104**, 1 (1943); Aleksandrov and Lazurkin, *Acta Physicochim.* (*U.S.S.R.*) **12**,, 647 669 (1940).
[22] According to the concept held by the present author regarding the structure of rubber, these mechanisms are the result of a large number of intermolecular bonds of unstable character, which exist in addition to the stable system of sulfur bridges formed by vulcanization, and are fewer in number.
[23] On this subject, see Kuhn, *Z. angew. Chem.* **52**, 289 (1939).
[24] Brennschede, *Kolloid-Z.* **104**, 1 (1943).
[25] Kuhn, *Z. angew. Chem.* **52**, 292 (1939).

THE STATISTICAL LENGTH OF LONG-CHAIN MOLECULES *

L. R. G. Treloar

The problem of determining the statistical distribution of "displacement length", *i.e.*, end-to-end distance, of a long-chain molecule of given chain length is one of fundamental importance in the development of the theory of elasticity for rubberlike materials. Distribution functions for the paraffin[1] and polyisoprene[2] (natural rubber) chains have been published by the author in papers which will be referred to subsequently as I and II respectively. The method used depended on processes carried out graphically, no method having been discovered of treating the statistics of these molecules in precise analytical terms.

The simplest "molecular" structure which can be considered from the analytical standpoint is the chain of universally jointed equal links, and, as pointed out in I, an accurate solution to the problem of the statistical distribution of length for such a chain may be obtained when the number of links is small, *e.g.* ~6, by a method due to Rayleigh[3]. The method is impracticable when the number of links is large.

In the present paper a formula is derived which is applicable to much longer chains This is obtained by a simple transformation of the result worked out by Hall[4] and Irwin[5] in 1927 in connection with the theory of random sampling. The relevance of the Hall-Irwin formula to the present problem was brought to the attention of the author by A. D. Booth of these laboratories.

The formula has been applied to chains of 25 and 100 links, and the resultant distribution curves are compared with those previously derived for the polyisoprene chain. The application of the results to the determination of the stress-strain relations of rubber will be considered in the following paper.

THE x-DISTRIBUTION FOR A RANDOM CHAIN

Let the chain be composed of n links, each of length l, such that each link is equally likely to be in any direction in space[6]. The distance between the ends of the chain is denoted by r, and the projection of r on a fixed line OX by x. It is required ultimately to find the distribution of r-values. As an intermediate step the distribution of x-values will be obtained.

By Equation (12) of I the probability that a single link has a component along OX between x and $x + \mathrm{d}x$ is given by:

$$p_1(x)\mathrm{d}x = \frac{\mathrm{d}x}{2l} \qquad (|x| < l) \tag{1}$$

i.e., the probability is constant over the range $-l$ to $+l$ and zero[1] elsewhere. A distribution of this type may be referred to as a "rectangular population". The x-component for the whole chain, which is the algebraical sum of the

* Reprinted from the *Transactions of the Faraday Society*, Vol. 42, Nos. 1 and 2, pages 77–82, January-February 1946.

separate x-components for the individual links, is therefore the sum of n values of x chosen at random from the population represented by (1).

The problem of finding the x-distribution for the whole chain is therefore equivalent to finding the distribution of the mean of n samples chosen at random from a rectangular population. For the mean is given by:

$$m = \frac{1}{n} \sum_{\mathrm{i}} x_{\mathrm{i}}$$

and in the present problem we require the total x-component for the chain which is:

$$x = \sum_{\mathrm{i}} x_{\mathrm{i}} = nm$$

The solution to this problem in statistics has been derived by Hall[4] and by Irwin[5] and is discussed briefly by Kendall[7]. The formula obtained by these authors gives the distribution of the mean of n samples from a rectangular population extending from $-\frac{1}{2}$ to $+\frac{1}{2}$ (*i.e.* corresponding to a link of length $\frac{1}{2}$), and is set out below:

$$f(m)\mathrm{d}m = \frac{n^n}{(n-1)!} \sum_{s=0}^{k} (-1)^s \binom{n}{s} \left(m - \frac{s}{n} \right)^{n-1} \mathrm{d}m \qquad (2)$$

where k is defined by:

$$\frac{k}{n} \leqslant m \leqslant \frac{k+1}{n}$$

In this expression $f(m)$ is the probability that the mean has the value m, and $\binom{n}{s}$ represents the number of combinations of n things taken s at a time. It will be seen that the function $f(m)$ is represented by n arcs making contact at the successive points given by $m = k/n$. Both $f(m)$ and its first derivative are continuous functions. The function $f(m)$ is symmetrical about the ordinate $m = \frac{1}{2}$, and extends from $m = 0$ to $m = 1$.

To adapt this solution to the case of the chain it is only necessary to remember that what we require is the total x instead of the mean. The transformation is effected by putting $m = \frac{1}{2}(1 - x/nl)$, thus spreading the distribution out in the ratio $2nl$ along the axis of abscissae and moving the origin to the position of the central maximum. At the same time the ordinates are reduced in the ratio $1/2nl$ so as to maintain unit area under the curve. The result is:

$$p(x)\mathrm{d}x = \frac{1}{2l} \frac{n^{n-1}}{(n-1)!} \sum_{s=0}^{k} (-1)^s \binom{n}{s} \left(m - \frac{s}{n} \right)^{n-1} \mathrm{d}x \qquad (3)$$

where

$$\frac{k}{n} \leqslant m \leqslant \frac{k+1}{n} \qquad \text{and} \qquad m = \tfrac{1}{2}(1 - x/nl)$$

THE r-DISTRIBUTION FUNCTION

To find the distribution of displacement length r we note that for chains of a given length r the corresponding distribution of x-values is given by an expression comparable with Equation (1), *i.e.*:

$$p_2(x)\mathrm{d}x = \frac{\mathrm{d}x}{2r} \qquad |x| < r$$

in which the limits of x are determined by r. In a continuous distribution of r-values, those chains whose r-values exceed a given (positive) value x will contribute to $p(x)$, while those for which $r < x$ make no contribution to $p(x)$. Hence the change in $p(x)$ over the range dx will be proportional to the number of chains whose r-values lie between x and dx. In mathematical terms:

$$-\left[\frac{dp(x)}{dx}\right]_{x=r} = \frac{1}{2r}P(r) \tag{4}$$

where $P(r)$ is the probability of a displacement length r. In this expression the positive half only of the symmetrical function $p(x)$ is considered, hence the factor $\frac{1}{2}$ is introduced on the right-hand side.

Application of (4) to the function (3) gives:

$$P(r)dr = \frac{r}{2l^2}\frac{n^{n-2}}{(n-2)!}\sum_{s=0}^{k}(-1)^s\binom{n}{s}\left(m-\frac{s}{n}\right)^{n-2}dr \tag{5}$$

where

$$\frac{k}{n} \leqslant m \leqslant \frac{k+1}{n} \qquad \text{and} \qquad m = \tfrac{1}{2}(1 - r/nl)$$

This is the exact distribution function covering the whole range of r. To illustrate the use of this formula, we may consider the case $n = 6$. We then have:

$$P(r) = \frac{27r}{l^2}\sum_{s=0}^{k}(-1)^s\binom{6}{s}\left(m-\frac{s}{6}\right)^4$$

giving for the 3 separate regions of r:

$$P(r) = \frac{27r}{l^2}\left(\frac{1}{2}-\frac{r}{12l}\right)^4 \qquad 4l \leqslant r \leqslant 6l,\ k = 0$$

$$P(r) = \frac{27r}{l^2}\left[\left(\frac{1}{3}-\frac{r}{12l}\right)^4 - 6\left(\frac{1}{3}-\frac{r}{12l}\right)^4\right] \qquad 2l \leqslant r \leqslant 4l,\ k = 1$$

$$P(r) = \frac{27r}{l^2}\left[\left(\frac{1}{2}-\frac{r}{12l}\right)^4 - 6\left(\frac{1}{3}-\frac{r}{12l}\right)^4 + 15\left(\frac{1}{6}-\frac{r}{12l}\right)^4\right]$$

$$0 \leqslant r \leqslant 2l,\ k = 2 \tag{6}$$

These expressions, when reduced, are identical with those derived by Rayleigh[3] by an entirely different method.

The functions $p(x)$ and $P(r)$ have been numerically evaluated for chains of 25 and 100 links each of unit length and the results are given in Tables I and II. For $n = 100$ the calculations were carried out by the Scientific Computing Service, for whose coöperation the author is indebted.

The form of the r-functions for $n = 25$ and $n = 100$ is shown in Figure 1, in which log $P(r)$ is plotted against $(r/r_m)^2$, $r_m(=nl)$ being the length of the fully-extended chain. Certain features of these functions are worthy of attention[7], namely:

(1) When r is small, the curves approximate to the "normal" or Gaussian distribution, represented by the equation:

$$P(r) = \frac{4\beta^3}{\pi^{\frac{1}{2}}}r^2e^{-\beta^2r^2} \qquad (\beta^2 = 3/2nl^2) \tag{7}$$

which is shown for comparison in Figure 1.

TABLE I

x AND r DISTRIBUTION

For 25-link Random Chain			*For 100-link Random Chain—Cont.*		
x or r	$\log_{10} p(x)$	$-\log_{10} P(r)$	x or r	$\log_{10} p(x)$	$-\log_{10} P(r)$
1	0.89	1.51	22	4.342	2.867
3	1.10	0.77	26	5.631	4.006
5	1.51	0.73	30	7.155	5.400
7	2.14	1.06	34	8.925	7.054
			38	10.955	8.978
9	3.01	1.69			
11	4.14	2.63	42	13.261	11.187
13	5.57	3.89	46	15.864	13.70
15	7.37	5.53	50	18.79	16.54
			54	22.07	19.74
17	9.66	7.65	58	25.76	23.34
19	12.64	10.46			
21	16.87	14.47	62	29.90	27.40
23	24.09	21.35	66	34.57	31.99
			70	38.89	37.22
			74	46.01	43.26
For 100-link Random Chain			78	53.18	50.33
2	1.187	1.806	82	61.80	58.85
6	1.395	1.061	86	72.61	69.52
10	1.811	1.034	90	87.07	83.82
14	2.437	1.366	94	109.04	105.54
18	3.279	1.984	98	156.27	152.28

TABLE II

No. of isoprene units in chain	Slope $n-2$	n	$\frac{n}{\text{No. of isoprene units}}$
32	44.0	46.0	1.437
64	90.4	92.4	1.443
128	184	186	1.452
256	369	371	1.448

(2) When r is large, *i.e.* $r > 0.7r_m$, only the first term ($s = 0$), of the summation in (5) is important, so that:

$$\frac{1}{r} P(r) \propto m^{n-2} \propto (1 - r/r_m)^{n-2} \tag{8}$$

(3) The general form of the function $P(r)$ is relatively insensitive to n, the number of chain-links.

COMPARISON WITH PARAFFIN AND POLYISOPRENE CHAINS

There is a close similarity between the distribution functions for the randomly jointed chain of equal links and those previously obtained for the paraffin and polyisoprene structures. In Figure 1, the distribution function for the 64-isoprene chain, represented by discrete points, is shown for comparison.

A more striking comparison is obtained by plotting $\log \frac{1}{r} P(r)$ against $\log (1 - r/r_m)$, which, when r is large, gives a straight line of slope $n - 2$ in the case of a random chain (see Equation (8)). From Figure 2 it is seen that this comparatively simple law holds approximately also for the polyisoprene

chains. Assuming for the moment that the polyisoprene chain may be replaced by a random chain of a suitable number of links, then the equivalent number of links may be obtained from the slopes of these logarithmic plots The results are given in Table II.

From the shape of the distribution at high r-values we are thus led to the conclusion that in this region, for all chain lengths, each isoprene unit is equivalent to about 1.44 random links.

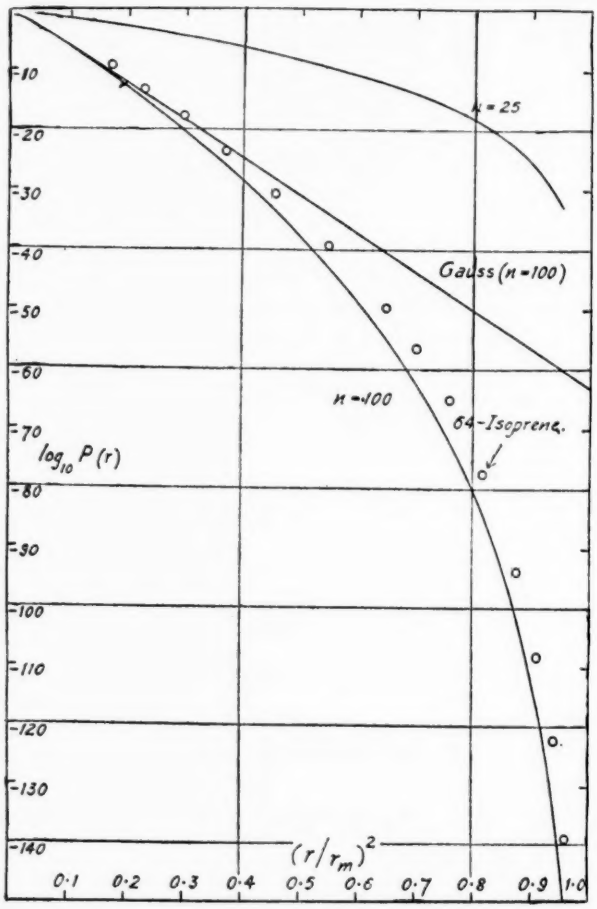


FIG. 1.—The distribution function for random chains of 2 and 100 links each of unit length. The function degenerates to the Gaussian form when r is small. The circles refer to the distribution for a polyisoprene chain of 64 isoprene units.

Another way of obtaining the number of links in the equivalent random chain (if such there be) is to consider the exponent β^2 in the Gaussian approximation (7) for small r. Wall's formula[8] for the mean square length $\overline{r^2}$ of the polyisoprene chain leads to the value:

$$\overline{r^2} = 3.72Z \text{ (A.}^2\text{)}$$

Z being the total number of bonds. For a 64-isoprene chain $Z = 256$, and since $r^2 = 3/2\beta^2$ we obtain for β^2 the value[9] of 0.00157. The maximum length r_m for the 64-isoprene chain is 294 A.

For a random chain of n links, each of length l, $\beta^2 = 3/2nl^2 = 3n/2r_m^2$. Hence, to find the equivalent number of links in the random chain having the same maximum length r_m as the 64-isoprene chain, we put $r_m = 294$ A. in the

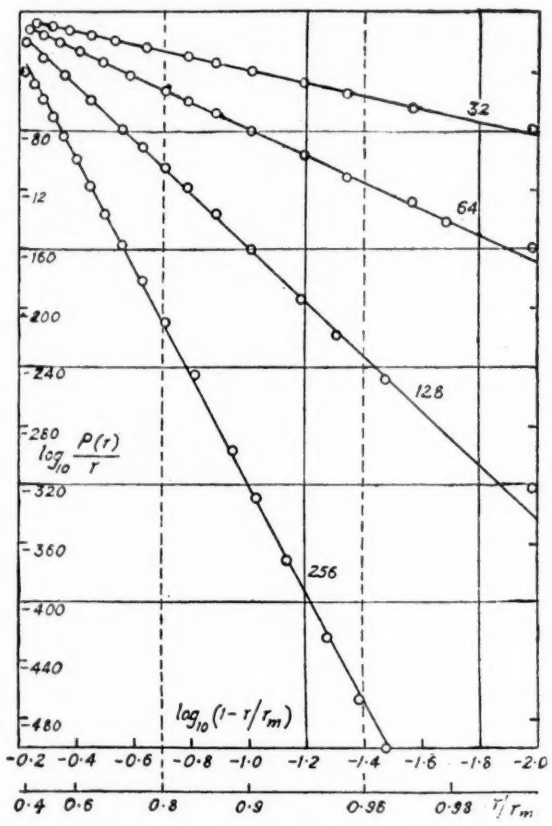


FIG. 2.—Plot of $\log \frac{1}{r}P(r)$ against $\log\ (1 - r/r_m)$ for polyisoprene chains of 32, 64, 128 and 256 isoprene units, showing that $P(r)$ approximates to the same form as in the case of random chains.

above expression. The result is $n = 90.5$, or 1.42 links per isoprene unit. This compares favorably with $n = 92.4$ obtained from the high-r region.

We conclude therefore that *a long polyisoprene chain is statistically equivalent over the whole range of extension to a random chain containing about* 1.42 *links for each isoprene unit.*

The paraffin chain is not quite so straightforward. The 80-link paraffin again gives a linear plot of $\log P(r)/r$ against $\log\ (1 - r/r_m)$ the slope being 34.5, corresponding to $n = 36.5$. From the value of β^2 in the Gaussian region, however, the value obtained for n for a chain of the same fully-extended length is 26.7. The discrepancy is rather large, and must be taken to mean that the

paraffin chain is not statistically equivalent to a random chain over the whole range of extension.

It cannot therefore be assumed that any chain-like structure will approximate statistically to the random chain of equal links over the whole range of r. The fact of this approximation in the case of the polyisoprene chain is a result of its particular geometrical structure.

SUMMARY

A formula is derived for the complete function representing the probability of a given distance between the ends of a chain of universally jointed equal links. The formula is computed for chains of 25 and 100 links. The distribution functions derived from this formula are compared with those previously worked out by an independent method for polyisoprene and paraffin chains. It is shown that the polyisoprene chain is statistically equivalent to a randomly-jointed chain of length corresponding to 1.42 links per isoprene unit.

This work forms part of a program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

[1] Treloar, *Proc. Phys. Soc.* **55**, 345 (1943).
[2] Treloar, *Trans. Faraday Soc.* **40**, 109 (1944).
[3] Rayleigh, *Phil. Mag.* **37**, 321 (1919).
[4] Hall, *Biometrika* **19**, 240 (1927).
[5] Irwin, *Biometrika* **19**, 225 (1927).
[6] By this is meant that if the successive links are represented by vectors radiating from a point, the end points of these vectors, on the average, will be uniformly distributed over the surface of a sphere.
[7] Kendall, "Advanced Statistics", Griffin & Co., 1943, Vol. 1, p. 240.
[8] Wall, *J. Chem. Physics* **11**, 67 (1943).
[9] This differs from the value of 0.001325 in II on account of the approximations involved in the previous method, which are discussed in the paper.

THE ELASTICITY OF A NETWORK OF LONG-CHAIN MOLECULES. III *

L. R. G. TRELOAR

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, WELWYN GARDEN CITY, HERTS, ENGLAND

In the second paper of this series[1] the statistical theory of Wall was developed to take account of the most general type of homogeneous deformation of a rubber, and a simple equation was derived giving the free energy of deformation in terms of the three principal strains. It was pointed out that this equation would not be expected to apply to a real rubber when any of the principal strains was very large, owing to the fact that the formula for the distribution of molecular lengths, on which it is based, is no longer applicable if an important fraction of the molecules are extended to a point approaching their maximum outstretched length. Later experimental work[2] confirmed that the theoretical equations were in reasonably good agreement with experimental data at small or moderate strains, but not at very large strains.

To extend the theory to cover the whole range of possible strains which can be applied to rubber, it is necessary to make use of the more accurate distribution functions which have since been worked out[3]. It is the purpose of the present paper to show how this may be achieved, and to present theoretical curves which represent the stress-strain properties of an ideal rubber over the whole range of deformations. It is not possible to derive a general algebraical equation covering any type of strain, as was done for the simpler case of small or moderate strains, but it appears to be necessary to work out each type of strain in detail. The types of strain considered are the simple elongation and 2-dimensional extension (or compression).

Two possible lines of attack on the problem of incorporating the effect of the "non-Gaussian" probability distributions of molecular length (or, briefly, "non-Gaussian chains") were considered. The first was on the basis of Wall's theory[4], and the second on the basis of Flory and Rehner's later theory[5]. The former was not proceeded with, on account of certain difficulties to which no very satisfactory solution was found. It will be sufficient to indicate here that these difficulties were mainly associated with the problem of how to formulate the distribution of chain lengths corresponding to the deformed state. It can no longer be assumed that the chain components change on deformation in the same ratio as the bulk rubber, as was done in the case of Gaussian chains.

Flory and Rehner's model, on the other hand, involves the introduction of no new principle, when applied to non-Gaussian chains, and for this reason was chosen as a basis for the present work.

Before the non-Gaussian case is considered, the original analysis of Flory and Rehner for Gaussian chains will be extended and generalized. It will be shown that the model leads to the same general equation for the free energy of deformation as had previously been obtained on the basis of Wall's theory.

* Reprinted from the *Transactions of the Faraday Society*, Vol. 42, Nos. 1 and 2, pages 83–94, January–February 1946.

THE FLORY-REHNER MODEL FOR GAUSSIAN CHAINS

The Flory-Rehner method involves the calculation of the entropy of formation of a network of molecules of equal contour or chain length. Four chains are assumed to radiate from each point of cross-linkage, and it is assumed that the restraints imposed on any given junction point by the remainder of the network will not be affected by fixing the four nearest-neighbor junction points at their average positions, *i.e.*, at the corners of a regular tetrahedron, Figure 1. It is further assumed that the mechanical properties of the network can be computed from those of this "average" cell of four chains, and that the dimensions of this cell are changed by the deformation in the same ratio as the dimensions of the bulk rubber.

The significant step in the calculation of the entropy of formation, in connection with the present problem, is that which concerns the junction of the four chains converging from the fixed corners of the tetrahedron. The prob-

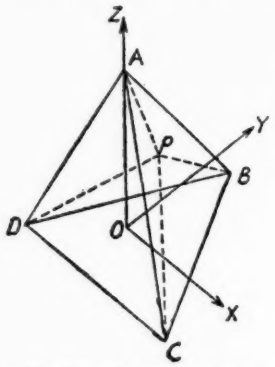


FIG. 1.—The Flory-Rehner tetrahedral model.

ability that these four chains should meet in a given small volume, $\Delta\tau = dx\,dydz$ may be written[6]:

$$\omega(x, y, z)(dx\,dy\,dz)^4 = \prod_{i=1}^{4} W(x_i\,y_i\,z_i)\,dx_i\,dy_i\,dz_i \qquad (1)$$

where $x_i\,y_i\,z_i$ are the coördinates of the same volume element $\Delta\tau$ referred, respectively, to the four corners A, B, C, D of the tetrahedron. For Gaussian chains we have:

$$W(x, y, z) = \frac{\beta^3}{\pi^{\frac{3}{2}}}\,e^{-\beta^2(x^2+y^2+z^2)}dx\,dy\,dz \qquad (2)$$

and in this special case, Equation (1) reduces to the form:

$$\omega(x, y, z) = \frac{\beta^{12}}{\omega^6}\exp\left[-\beta^2\sum_{i=1}^{4} r_i^2\right] \qquad (3)$$

The quantity Σr_i^2 has to be evaluated at all points of space. Integration then gives the probability of the four chains meeting anywhere in space and consequently the entropy corresponding to the formation process. This entropy is calculated both for the stretched and unstretched states. The difference is the required entropy of deformation.

Flory and Rehner consider the application of a simple elongation α in two special directions with respect to the cell, namely along OY and OZ (Figure 1) and show that the resultant entropy is the same in each of these cases. They point out that, strictly, an average should be taken over all possible directions of the elongation, but make the reasonable assumption that the result obtained for the two special directions may be taken to represent this average.

In the following treatment, Flory and Rehner's analysis will be extended in two ways, namely:

(1) By the application of the most general type of homogeneous deformation, and

(2) By establishing that the entropy of deformation is the same for all possible directions of the principal strains with respect to the tetrahedral cell.

Suppose the positions of the corners A, B, C, D to be defined originally with respect to the coördinate system OX, OY, OZ, the origin being at the center of the tetrahedron, OX parallel to DC and OZ perpendicular to the plane BCD. The average length of each chain in the undeformed state is $OA = \lambda$.

The general homogeneous deformation may be described by stretches in the ratio α_1, α_2 and α_3 in three mutually perpendicular directions, OX′, OY′, OZ′—the principal axes of strain. It will be assumed that these axes are related to OX, OY, OZ by the direction cosines (l_1, m_1, n_1), (l_2, m_2, n_2), (l_3, m_3, n_3), respectively. If a point P has coördinates (x, y, z) referred to OX, OY, OZ, its coördinates (x', y', z') referred to OX′, OY′, OZ′ are given by the relations:

$$\begin{aligned} x' &= l_1x + l_2y + l_3z \\ y' &= m_1x + m_2y + m_3z \\ z' &= n_1x + n_2y + n_3z \end{aligned}$$

The coördinates of the points A, B, C, D in the strained state, referred to OX′, OY′, OZ′ may thus be shown to be the following:

For A:

$$x_1/\lambda = \alpha_1 l_3,\ y_1/\lambda = \alpha_2 m_3,\ z_1/\lambda = \alpha_3 n_3$$

For B:

$$\begin{aligned} x_2/\lambda &= (2\sqrt{2}l_2/3 - l_3/3)\alpha_1 \\ y_2/\lambda &= (2\sqrt{2}m_2/3 - m_3/3)\alpha_2 \\ z_2/\lambda &= (2\sqrt{2}n_2/3 - n_3/3)\beta_3 \end{aligned}$$

For C:

$$\begin{aligned} x_3/\lambda &= (\sqrt{2}l_1\sqrt{3} - \sqrt{2}l_2/3 - l_3/3)\alpha_1 \\ y_3/\lambda &= (\sqrt{2}m_1/\sqrt{3} - \sqrt{2}m_2/3 - m_3/3)\alpha_2 \\ z_3/\lambda &= (\sqrt{2}n_1/\sqrt{3} - \sqrt{2}n_2/3 - n_3/3)\alpha_3 \end{aligned}$$

For D:

$$x_4/\lambda = (-\sqrt{2}l_1/\sqrt{3} - \sqrt{2}l_2/3 - l_3/3)\alpha_1, \quad \text{etc.}$$

We have now to take any point P, having coördinates (x', y', z') and find $\Sigma r_i^2 = PA^2 + PB^2 + PC^2 + PD^2$ (see Equation (3)).

$$\begin{aligned} PA^2/\lambda^2 &= (x'/\lambda - l_3\alpha_1)^2 + (y'/\lambda - m_3\alpha_2)^2 + (z'/\lambda - n_3\alpha_3)^2 \\ PB^2/\lambda^2 &= [x'/\lambda - (2\sqrt{2}l_2/3 - l_3/3)\alpha_1]^2 + \cdots \\ PC^2/\lambda^2 &= [x'/\lambda - (\sqrt{2}l_1/\sqrt{3} - \sqrt{2}l_2/\sqrt{3} - l_3/3)\alpha_1]^2 + \cdots \\ PD^2/\lambda^2 &= [x'/\lambda + (\sqrt{2}l_i/\sqrt{3} + \sqrt{2}l_2/\sqrt{3} - l_3/3)\alpha_i]^2 + \cdots \end{aligned}$$

so that

$$\frac{1}{\lambda^2}\Sigma r_i^2 = 4x'^2/\lambda^2 + 2\alpha_1 x'[-l_3 - (2\sqrt{2l_2/3} - l_3/3) - (\sqrt{2l_1/\sqrt{3}} - \sqrt{2l_2/3} - l_3/3) + (\sqrt{2l_1/\sqrt{3}} + \sqrt{2l_2/3} - l_3/3)] + \alpha_1^2[l_3^2 + (2\sqrt{2l_2/3} - l_3/3)^2 + (\sqrt{2l_1/\sqrt{3}} - \sqrt{2l_2/3} - l_3/3)^2 + (\sqrt{2l_1/\sqrt{3}} + \sqrt{2l_2/3} + l_3/3)^2]$$

+ similar expressions in y' and z', leading to

$$\Sigma r_i^2 = 4x'^2 + \tfrac{4}{3}\alpha_1^2\lambda^2(l_1^2 + l_2^2 + l_3^2) + \cdots = 4[(x'^2 + y'^2 + z'^2) + \lambda^2(\alpha_1^2 + \alpha_2^2 + \alpha_3^2)/3]$$

since

$$l_1^2 + l_2^2 + l_3^2 = 1, \quad \text{etc.}$$

Thus

$$\Sigma r_i^2 = 4[s^2 + \lambda^2(\alpha_1^2 + \alpha_2^2 + \alpha_3^2)/3] \tag{4}$$

where s is the distance of P from the origin.

Equation (4) replaces Equation (17) in Flory and Rehner's paper[5]. If this is inserted in Equation (3) and the integration is carried out in the manner described in their paper, taking $\lambda^2 = 3/2\beta^2$ the expression for the entropy of deformation becomes:

$$\Delta S = -\tfrac{1}{2}N\boldsymbol{k}(\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - 3) \tag{5}$$

in which N is the number of molecular chains. The entropy of deformation is thus proved to be independent of the direction cosines of the principal axes of strain. Flory's expression (19′) is a special case of the more general form (5), obtained by putting $\alpha_1 = \alpha$, $\alpha_2 = \alpha_3 = \alpha^{-\frac{1}{2}}$. The free energy of deformation, W, is obtained directly from (5), *i.e.*:

$$W = \tfrac{1}{2}N\boldsymbol{k}T\,(\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - 3) \tag{6}$$

This formula is identical with that derived in II on the basis of Wall's theory. In the previous derivation, however, it was necessary to assume that the volume remained constant under deformation. This assumption is not involved in the present argument.

Having now established the equivalence of the methods of Flory and Rehner and of Wall with regard to Gaussian chains, and having shown that the geometrical relation of the elementary cell to the axes of strain makes no difference to the results, we may proceed with more confidence to the application of Flory and Rehner's model to the more complex case of non-Gaussian chains.

THE FLORY–REHNER MODEL FOR NON-GAUSSIAN CHAINS

The only difference involved in the application to non-Gaussian chains is that in place of the distribution represented by Equation (2), we have:

$$W(x, y, z) = \frac{1}{4\pi r^2}P(r)$$

where $P(r)$ is the distribution function for the random chain, evaluated in the preceding paper[3]. In the non-Gaussian region Equation (1) no longer reduces to (3), and consequently $\omega(x, y, z)$ is not simply a function of Σr_i^2.

In principle, it is necessary to find $\omega(x, y, z)$, which is the product of the separate probabilities that each of the four chains should terminate in the volume element at P, at all points in space, and to integrate over the whole volume. The result would give the required probability of the four chains meeting anywhere in space. If it was desired to obtain a complete stress-strain relation, it would be necessary to carry out this calculation at a number of different strains.

Such a procedure might well appear impossibly laborious, but in practice it is possible to introduce approximations which greatly reduce the amount of work involved. The principle adopted was to locate by trial the point at which the probability density $\omega(x, y, z)$ was a maximum, and then to explore the variation of ω along the directions of the three coördinate axes, taking this point as origin. In the case of Gaussian chains, as will be seen from Equation (4), the point of maximum probability density is at the center of the tetrahedron, and the variation of ω may be expressed in terms of the maximum probability density ω_0 and the distance s from the center by the Gaussian formula:

$$\omega = \omega_0 e^{-4\beta^2 s^2} \tag{7}$$

which shows the variation of probability to be spherically symmetrical and independent of strain. For non-Gaussian chains, on the other hand, it is found, when the calculations are carried out, that the variation is no longer spherically symmetrical. The variation along any one direction, however, remains approximately Gaussian, even though the rate of fall is different along the three directions chosen. In this way there are obtained three equations of the type:

$$w_x = \omega_0' e^{-4\beta_1^2 x^2} \tag{8}$$

From (7) the total probability, in the Gaussian case, is proportional to:

$$\Omega = \omega_0 \int 4\pi s^2 e^{-4\beta^2 s^2} ds = \omega_0 \cdot \frac{\pi^{\frac{3}{2}}}{8\beta^3} \tag{9}$$

The comparable expression for the non-Gaussian case was assumed to be:

$$\Omega' = \omega_0' \frac{\pi^{\frac{3}{2}}}{8\beta_1\beta_2\beta_3} \tag{10}$$

corresponding to an ellipsoidal distribution of probability density. The entropy change in deformation is thus dependent on two terms, *i.e.:*

$$\frac{\Delta S}{k} = \ln \frac{\omega_0'}{\omega_0} - \ln \frac{\beta^3}{\beta_1\beta_2\beta_3} \tag{11}$$

of which the first represents the probability at the maximum, which may be called the "intensity factor", while the second, or "volume factor" represents the rate at which the probability falls away on moving outwards from the maximum.

The foregoing analysis of the spatial distribution of probability density, though admittedly only approximate, is quite adequate for the purpose. The reason is that the second term in (11) is found to be, in all cases, very small compared with the first. Thus for 25-link chains, the "volume factor" never accounted for more than 3 per cent of the total entropy change, while for 100-link chains its maximum contribution was always less than 1 per cent of the

whole. The amount of work involved in calculating the spatial distribution, even in this approximate manner, is thus justified rather by the desire for theoretical completeness than on account of its practical significance.

SIMPLE ELONGATION

In the non-Gaussian case it is no longer true that the entropy change will be independent of the direction of the elongation with respect to the tetrahedron, and the choice of this direction has to be made arbitrarily. A few calculations were, however, made, from which some idea of the effect of stretching in other directions may be obtained.

The stretching direction chosen was along OX (Figure 1). The corners of the tetrahedral cell were assumed to move in such a way that their x-coördinates changed in the ratio α, while their y- and z-coördinates changed in the ratio $\alpha^{-\frac{1}{2}}$. The entropy was calculated at a number of values of α. For the Gaussian region this entropy has the value $-2k(\alpha^2 + 2/\alpha - 3)$; it is convenient, therefore, to express the calculated entropy ΔS in the form of the ratio which it bears to the quantity $2k(\alpha^2 + 2/\alpha - 3)$. These ratios are given in Table I.

TABLE I

SIMPLE ELONGATION

Calculated values of $\Delta S/2k(\alpha^2 + 2/\alpha - 3)$ for 4-chain cell. $n = 25$ and 100.

$n = 25$		$n = 100$	
α	$\frac{-\Delta S}{2k(\alpha^2 + 2/\alpha - 3)}$	α	$\frac{-\Delta S}{2k(\alpha^2 + 2/\alpha - 3)}$
1.5	1.00_0	2.0	1.00_0
2.0	1.02_0	2.5	1.00_6
2.5	1.04_6	3.0	1.01_7
3.0	1.07_4	4.0	1.03_2
3.5	1.11_4	5.0	1.05_4
4.0	1.16_7	6.0	1.08_3
4.5	1.25_2	7.0	1.12_4
4.75	1.31_0	8.0	1.17_9
5.0	1.38_2	9.0	1.25_5
5.25	1.48_0	10.0	1.39_4
5.5	1.63	11.0	1.63
5.75	1.88	11.5	1.89
5.85	2.03		

It is interesting to notice that the functions $\Delta S/2k(\alpha^2 + 2/\alpha - 3)$ for the two different chain lengths are of similar form, and differ only in the range of α covered. Especially is this true when α is large, the value of the function for $n = 25$ at a given value of α being almost exactly the same as for $n = 100$ and twice that value of α. This property would be useful if it were required to interpolate for other values of n.

The tensile force is proportional to $-\mathrm{d}\Delta S/\mathrm{d}\alpha$, and the most direct way of obtaining this is from the slope of the curve of ΔS plotted against α. However, it is more accurate to derive the force indirectly, from a plot of the above function $\Delta S/2k(\alpha^2 + 2/\alpha - 3)$ against α. If this function is denoted by σ it is easy to show that:

$$\frac{1}{k}\frac{\mathrm{d}\Delta S}{\mathrm{d}\alpha} = 2(\alpha^2 + 2/\alpha - 3)\frac{\mathrm{d}\sigma}{\mathrm{d}\alpha} + 4(\alpha - 1/\alpha^2)\sigma \qquad (12)$$

The values of $d\sigma/d\alpha$ were obtained by drawing a smooth curve through the points given in Table I, and finding its slope at these points. The advantage of this method is that $d\Delta S/d\alpha$ is obtained as the sum of two terms, of which only the first (which is generally the smaller) involves the slope taken from the curve. If F is the tensile force per square cm. of the original cross-section of the bulk rubber, and if N is the number of molecular chains per cc., we have then:

$$\frac{F}{NkT} = -\frac{1}{4k}\frac{d\Delta S}{d\alpha} \tag{13}$$

since the tetrahedron contains four chains.

The functions F/NkT are reproduced in Figure 2.

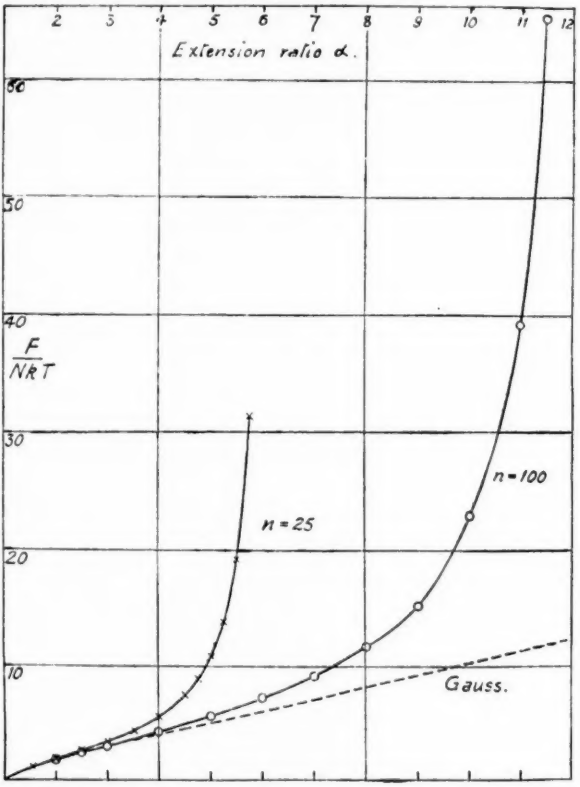


FIG. 2.—Simple elongation. The function F/NkT for a network of random chains of 25 and 100 links.

Effect of Different Directions of Extension.—Differences between different directions of extension become increasingly significant with increasing extension. However, these differences affect only the detail of the stress-strain curve, and not its general shape. For the z-direction, which differs most seriously from the x-direction, the value of $\Delta S/k$ at $\alpha = 5.5$, $n = 25$, was found to be 80.5 compared with 89.8 for the x-direction. The same value of $\Delta S/k$ (80.5) would be given a stretch of about $\alpha = 5.37$ in the x-direction.

This indicates the kind of maximum divergence between the different directions of stretching. Since, ideally, it is the average entropy for stretching in all directions which is required, it is considered that any error introduced by considering only the x-direction is likely to be very slight.

TWO-DIMENSIONAL EXTENSION

In the 2-dimensional extension the x-dimension of the tetrahedron was reduced in the ratio α (where $\alpha < 1$), while the y and z dimensions were increased in the ratio $\alpha^{-\frac{1}{2}}$. As before, the entropy may conveniently be represented by $\Delta S/2k(\alpha^2 + 2/\alpha - 3)$ or σ which is given in Table II, as a function of the linear extension ratio $\alpha^{-\frac{1}{2}}$.

TABLE II

TWO-DIMENSIONAL EXTENSION

Calculated values of $\Delta S/2k(\alpha + 2/\alpha - 3)$ for 4-chain cell. $n = 25$ and 100.

$n = 25$		$n = 100$	
Linear extension ratio $1/\sqrt{\alpha}$	$\frac{-\Delta S}{2k(\alpha^2 + 2/\alpha - 3)}$	Linear extension ratio $1/\sqrt{\alpha}$	$\frac{-\Delta S}{2k(\alpha^2 + 2/\alpha - 3)}$
1.414	1.00_0	2.0	1.00_5
2.0	1.03_1	3.0	1.01_6
2.45	1.05_8	4.0	1.03_8
3.0	1.09_3	5.0	1.06_7
3.46	1.14_9	6.0	1.10_4
4.0	1.22_6	7.0	1.16_2
4.47	1.33_5	8.0	1.24_0
5.0	1.56	9.0	1.36_5
5.25	1.75	10.0	1.59
		10.5	1.78

Once again, it is seen that the entropy curves for the two chain lengths are very similar, but in the present case it is the scale of $\alpha^{-\frac{1}{2}}$ which is doubled on multiplying n by 4.

Since there is assumed to be no change of volume of the rubber, a strain of the kind considered may be regarded either as a unidirectional compression or as a 2-dimensional extension. From the entropy it is possible to calculate either the compressive force in the first case, or the tensile force in the second. For the compressive force, per sq. cm. of the original section, we have:

$$f = -T\mathrm{d}\Delta S/\mathrm{d}\alpha \tag{14}$$

The tensile force per cm. in a sheet of original thickness 1 cm., stretched in two dimensions is [2]:

$$t = \alpha^2 f \tag{15}$$

The second is the more convenient quantity for graphical representation.

The compression force is formally equivalent to the tensile force in a simple elongation, hence from (12) and (13):

$$-\frac{4f}{NkT} = 2(\alpha^2 + 2/\alpha - 3)\frac{\mathrm{d}\sigma}{\mathrm{d}\alpha} + 4(\alpha - 1/\alpha^2)\sigma$$

Hence, introducing (15), the tension in the equivalent 2-dimensional extension is:

$$-\frac{4t}{NkT} = 2\alpha^2(\alpha^2 + 2/\alpha - 3)\frac{\mathrm{d}\sigma}{\mathrm{d}\alpha} + 4(\alpha^3 - 1)\sigma \tag{16}$$

The quantity $d\sigma/d\alpha$ in this expression is not obtainable accurately from a direct plot of σ against α because of the rapid variation of σ with α. It is more satisfactory to plot σ against $\alpha^{-\frac{1}{2}}$ and thus to obtain $d\sigma/d(\alpha^{-\frac{1}{2}})$. This is converted to $d\sigma/d\alpha$ by the relation:

$$\frac{d\sigma}{d\alpha} = -\frac{1}{2\alpha^{\frac{1}{2}}} \cdot \frac{d\sigma}{d(\alpha^{-\frac{1}{2}})}$$

so that (16) becomes:

$$\frac{4t}{NkT} = \alpha^{\frac{1}{2}}(\alpha^2 + 2/\alpha - 3)\frac{d\sigma}{d(\alpha^{-\frac{1}{2}})} + 4(1 - \alpha^3)\sigma \qquad (17)$$

The result of the application of this equation is shown in Figure 3.

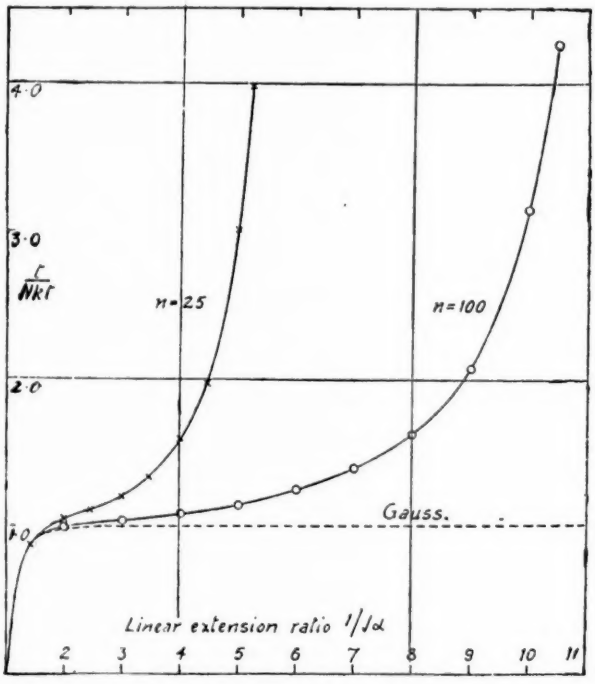


FIG. 3.—Two-dimensional extension. The function t/NkT for a network of random chains of 25 and 100 links.

APPLICATION TO POLYISOPRENE RUBBER

So far the work has been concerned with a network of randomly-linked chains. The resultant stress-strain relations, shown in Figures 2 and 3, give the stresses divided by NkT where N is the number of chains per cc.

To proceed further, in order to derive the actual stresses in kg. per sq. cm. on the rubber, it is necessary to find a way of introducing N numerically. For this purpose our mathematical chain must be given a mass. The quantity NkT is then equal to $\rho RT/M$, where M is the "molecular" weight of the chain. and ρ the density of the bulk rubber.

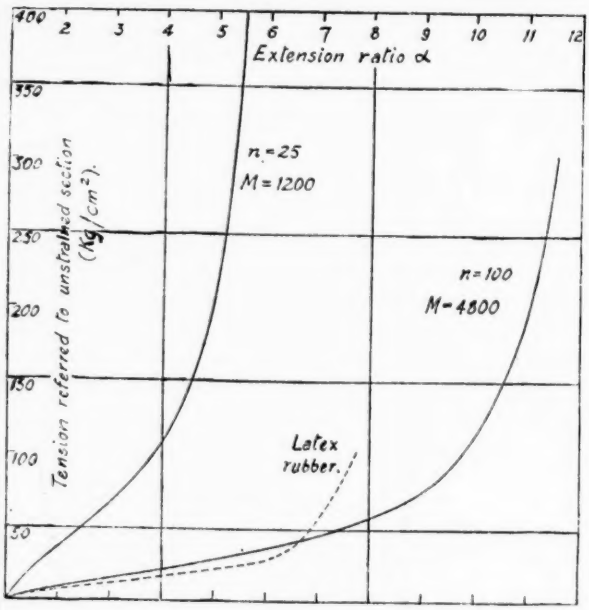


FIG. 4.—Simple elongation. Stress-strain curves for polyisoprene rubber. M = molecular weight between points of cross-linkage.

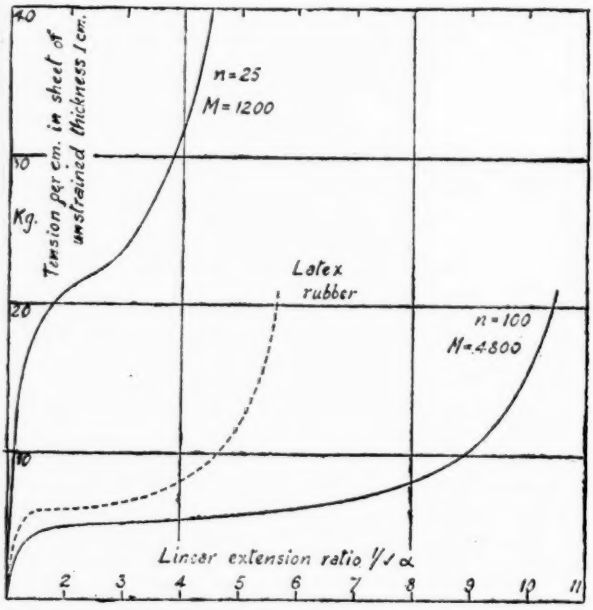


FIG. 5.—Two-dimensional extension. Stress-strain curve for polyisoprene rubber. M = molecular weight between points of cross-linkage.

For the appropriate value of M, the random chain may be compared with the polyisoprene chain. The last paper showed that the polyisoprene chain is statistically equivalent to a random chain of 1.42 links per isoprene unit. The 25-link random chain is therefore equivalent to a chain of 17.6 isoprene units, which would have a molecular weight of 1200. Similarly the 100-link random chain is equivalent to a polyisoprene of molecular weight 4800. Introduction of the appropriate factors gives, then, the force in kg. per sq. cm. The resulting curves are shown in Figures 4 and 5, for a temperature of 25° C.

COMPARISON WITH EXPERIMENT

In Figures 4 and 5 the experimental stress-strain relations for the latex rubber, reported in a previous paper[2], are plotted for comparison with the theoretical curves. The value of NkT for this rubber was 6.3, which corresponds to a "molecular" weight of 4100. (The temperature in these experiments was 50° C.) Its extensibility, for both simple and 2-dimensional extension, should therefore be about 8 per cent lower than for the theoretical rubber corresponding to $M = 4800$, since the extensibility varies approximately as the square root of the chain length. Its actual extensibility, judging by the position of the upward bend in the curve, appears to be about 80 per cent in the simple extension, and 55 per cent in the 2-dimensional extension, of the extensibility for the theoretical $M = 4800$, or about 87 and 60 per cent, respectively, of the theoretical for $M = 4100$.

These differences between the experimental and theoretical extensibilities are very much smaller than the author was led to expect from an earlier and very much cruder theoretical analysis[7].

GENERAL DISCUSSION

It may be useful to recall the assumptions on which the theoretical treatment of the problem of the elasticity of a network of long-chain molecules is based. These are (1) that the molecules are endowed with freedom of rotation about single bonds; (2) that the lengths of molecular chain between junction points are all the same; (3) that the properties of the rubber are correctly represented by a simple "cell" of four chains, whose average displacement length is the root-mean-square length of the free chain, and (4) that there is no change in internal energy on deformation at constant temperature, so that the work of deformation may be equated to the entropy. The additional assumption of no volume change on deformation is not really an assumption but a well-established experimental fact.

Given the geometrical construction of the molecular chains, which determines their statistical distribution of displacement length, it is possible, on the basis of the above four assumptions, to derive the stress-strain relationships for any type of strain. In this process, there is, for a given rubber, only one variable parameter—the chain contour length. This determines quantitatively both the vertical and horizontal scales. It is found that, for moderate strains the vertical scale, *i.e.*, stress, is inversely proportional to the chain contour length, while the horizontal range, or maximum strain is a function of the extensibility of the molecule, and for simple elongation or 2-dimensional extension is proportional to the square root of the chain length. Though the paper is concerned with the polyisoprene chain, these general properties will be the same for molecules of different geometrical construction. The general features of the stress-strain relations are fundamental and would be expected

from any form of network theory, since they are derived directly from the fundamental statistical properties of long-chain molecules. The exact form of the stress-strain curves, is, however, less firmly established, owing to the arbitrary features of a simplifying nature necessarily introduced in any chosen model. Thus, for example, the assumption that the nearest-neighbor junction points to a given junction point may be regarded as fixed in their average positions, and the difficulty, referred to by Flory and Rehner[5], of knowing which kind of average should be chosen in this connection, are arbitrary features which other possible models might avoid or improve on. The same applies also to the obviously inaccurate assumption that all the chains are of the same length.

A further source of error is connected with the derivation of the statistical distribution of molecular displacement lengths. In this derivation the volume occupied by the chain atoms has been neglected. If these defects were removed, the average chain displacement length would be increased, and since the maximum length would be unchanged, it follows that the extensibility of the molecule and consequently of the network would be reduced. This factor may very well be the main reason for the discrepancy between the experimental and theoretical extensibilities discussed above.

The difficulties are, however, not all on the theoretical side. The determination of a real equilibrium stress-strain curve for rubber is a matter of very considerable difficulty, particularly at large strains, where such effects as crystallization and mechanical relaxation are very serious. In the experimental curves shown in this paper it is not suggested that these effects have been eliminated, and their inclusion is justified only by the absence of any more satisfactory data. It might be thought possible to remove these experimental difficulties by working with a synthetic rubber which does not crystallize, but then one encounters the difficulty that such rubbers are invariably mechanically weak and do not permit the application of large strains. Also their precise molecular constitution is not, and cannot be known.

A further difficulty, of a related kind, lies in the fact that the deformation, particularly when large, may result in internal energy changes. Such changes may arise from the modification of the intermolecular forces by orientation (leading in the extreme case to crystallization) or from forces between the atoms of a single chain. Such changes may be estimated experimentally, and the contribution to the total free energy resulting from them may be subtracted so as to obtain the pure entropy change, as has been attempted by Anthony, Caston and Guth[8], but the experimental difficulties involved are here also likely to prove very serious at large strains.

For the reasons advanced in this paragraph, it is evident that caution must be exercised in making a quantitative comparison between the theoretical stress-strain curves and the experimental data available. In spite of the difficulties, however, it is clear that the theory leads to stress-strain relations comparable with the experimental curves in all their characteristic features. This is particularly well shown for the case of a 2-dimensional extension (Figure 5). It seems justifiable to conclude that the *main elastic properties of a well-vulcanized rubber, even at large strains, are related primarily (though not necessarily exclusively) to the statistical configurations of molecules in a 3-dimensional network.*

SUMMARY

The accurate functions representing the distribution of length of long-chain molecules are introduced into the Flory-Rehner model, by means of

which the mechanical properties of a network of such molecules, corresponding to a vulcanized rubber, may be calculated. Stress-strain curves are obtained for (1) simple elongation and (2) 2-dimensional extension, using chain lengths corresponding to polyisoprene rubbers of molecular weight (M) between junction points of the network of 1200 and 4800, respectively. These curves show all the essential features of the corresponding experimental curves for natural rubber right up to the breaking point, though the extensibility of the real rubber is significantly less than the theoretical. They show also that the stress for a given small or moderate deformation is inversely proportional to M, while the range of extensibility is directly proportional to $M^{\frac{1}{2}}$.

Though an exact agreement between the theoretical and experimental stress-strain relations is not to be expected, on account of the many difficulties encountered in matters of detail both on the theoretical and on the experimental side, the degree of agreement revealed is considered to warrant the conclusion that the main elastic properties of vulcanized rubber are essentially statistical properties of a network of long-chain molecules.

This work forms part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

[1] Treloar, *Trans. Faraday Soc.* **39**, 241 (1943).
[2] Treloar, *Trans. Faraday Soc.* **40**, 59 (1944).
[3] Treloar, *Trans. Faraday Soc.*, in press.
[4] Wall, *J. Chem. Physics* **10**, 485 (1942).
[5] Flory and Rehner, *J. Chem. Physics* **11**, 512 (1943).
[6] The notation of Flory and Rehner, has been slightly modified.
[7] Treloar, *Rept. Progress Physics* **9**, 113 (1943).
[8] Anthony, Caston and Guth, *J. Phys. Chem.* **46**, 826 (1942).

THE COURSE OF AUTOÖXIDATION REACTIONS IN POLYISOPRENES AND ALLIED COMPOUNDS. XI. DOUBLE-BOND MOVEMENT DURING THE AUTOÖXIDATION OF A MONOÖLEFIN *

E. HAROLD FARMER AND DONALD A. SUTTON

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, WELWYN GARDEN CITY, HERTS, ENGLAND

In an earlier part of this investigation[1] it was shown that the autoöxidation of $\Delta^{1,4}$-dienes and $\Delta^{1,4,7}$-, etc., polyene compounds produces peroxido derivatives containing conjugated units, and to explain the formation of the latter a reaction-mechanism was proposed which postulated the detachment of hydrogen atoms from the reactive methylene groups under the action of molecular oxygen, and subsequent rearrangement of the resonating radical residues before oxygen and, finally, hydrogen combine therewith to give hydroperoxides:

$$\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot \longrightarrow$$

$$\cdot CH{:}CH\cdot \overset{*}{C}H\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot \rightleftharpoons$$

$$\cdot \overset{*}{C}H\cdot CH{:}CH\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot \text{ or}$$

$$\cdot CH{:}CH\cdot CH{:}CH\cdot \overset{*}{C}H\cdot CH_2\cdot CH{:}CH\cdot \xrightarrow{O_2} \text{Hydroperoxides}$$

It was recognized that, if this mechanism is valid for methylene-interrupted diene or polyene systems, it might reasonably be expected to apply also to the formation of hydroperoxides by the action of oxygen either on simple olefins or on polyolefins containing two or more methylene groups between the double bonds. To demonstrate successfully that even the simplest olefin system capable of hydroperoxidation can give both of the oxygenated forms (A) and (B):

$$\cdot CH_2\cdot CH{:}CH\cdot \xrightarrow{-H} \cdot CH\cdots CH\cdots CH\cdot \xrightarrow[H]{O_2}$$

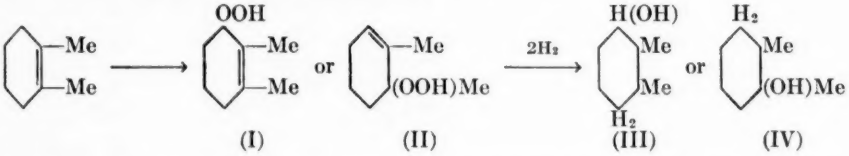
$$\underset{(A)}{\cdot CH(OOH)\cdot CH{:}CH\cdot} \text{ and } \underset{(B)}{\cdot CH{:}CH\cdot CH(OOH)\cdot},$$

it is necessary for practical reasons to fulfil three conditions, *viz.*, (1) the hydroperoxide(s) formed by autoöxidation must be sufficiently stable to survive in good yield until the required amount of oxygen has been absorbed, (2) the olefin selected must be of such convenient constitution that the task of distinguishing structurally between the expected isomeric hydroperoxides is not unduly difficult, and (3) the hydroperoxides formed must be capable of trans-

* Reprinted from the *Journal of the Chemical Society*, 1945, pages 10–13. This paper represents Publication No. 67 of The British Rubber Producers' Research Association.

formation into identifiable derivatives without undergoing too high a proportion of secondary change (*i.e.*, change involving isomerization by oxygen redistribution or oxidative degradation). Various of the simple olefinic substances so far used in our autoöxidation experiments, and especially the cyclohexenes as a group, satisfy the first condition, some few are able to satisfy the second, but few are found in practice to satisfy the third. For a first attempt, to demonstrate the occurrence of double bond shift during hydroperoxidation, 1,2-dimethyl-Δ^1-cyclohexene seemed most suitable, for, although the degree of its satisfaction of the third condition left a good deal to be desired—at any rate with respect to identification by hydrogenation—it successfully complied with the second in that its two alkyl groups could serve as reference points for recognizing double bond shift if it occurred, and also by their presence could prevent unwanted isomerism arising from hydroperoxidation at alternative methylene groups in the system $\cdot CH_2 \cdot CH:CH \cdot CH_2$.

The formation and rectification of the hydroperoxide of 1,2-dimethyl-Δ^1-cyclohexene has already been described by Farmer and Sundralingam[2]. An unexpected feature of the freshly distilled peroxide was that the peroxide content ($\cdot O \cdot O \cdot$) as measured by the colorimetric method of Bolland *et al.* which has usually been found to be very dependable for this type of peroxide, was considerably higher than the theoretical, but as measured by the potassium iodide method of Dastur and Lea[4] was considerably lower than the theoretical. When the peroxide had been kept for 5 days at 0°, the colorimetric value fell to near the theoretical, while the content as measured by the potassium iodide method fell somewhat also. The causes controlling the appearance of this phenomenon are not understood at present, but as the phenomenon has now been observed in connection with several other olefinic peroxides, it apparently means that some of the molecules of certain freshly distilled peroxides are able to use both of their oxygen atoms for the oxidation of ferrous sulfate and not only one as is normally the case. By use of a mixed platinum-palladium catalyst, which is usually more successful than platinum alone for peroxide reductions[6] the hydrogenation of the peroxide in the normal fashion could only be effected to the extent of about 75 per cent, and the product of this reaction was a mixture of alcohols having the required composition, $C_8H_{15}(OH)$. This mixture proved to consist of approximately equal amounts of the secondary alcohol (III) (isolated and identified), and of the tertiary isomer (IV), the presence of which was indicated by the production of 1,2-dimethyl-Δ^1-cyclohexene on dehydration by heat in the presence of traces of iodine.

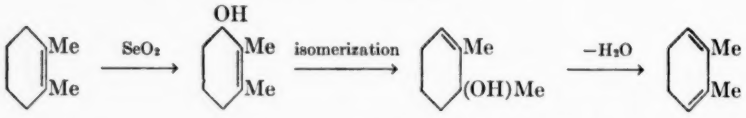


(I) (II) (III) (IV)

Thus, it may be inferred that the two hydroperoxides (I) and (II), *i.e.*, the structures which are to be expected in terms of the radical hydroperoxidation hypothesis, were both present in the oxidation product, and hence that the autoöxidation of simple olefins can actually be accompanied by a considerable degree of double bond shift.

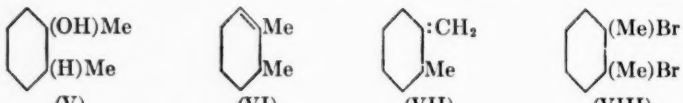
This demonstration of course depends for its validity on the absence of anionotropic interchange between the alcohols (III) and (IV), or between the formed hydroperoxide molecules (I) and (II), but since (1) the existing evidence

relating to the mechanism of peroxidation (expecially photoöxidation as here used) is overwhelmingly in favor of a radical chain-process, and (2) the experimental conditions of peroxidation and hydrogenation were not such as would promote the separation of anions, the occurrence of any significant degree of anionotropy seems unlikely. In the comparable case of the oxidation of 1,2-dimethyl-Δ^1-cyclohexene by selenium dioxide, the product from which was shown by Guillemonat[7] to contain the conjugated diene 1,2-dimethyl-$\Delta^{2,6}$-cyclohexadiene, formed in his view by the following steps:



the absence of anionotropy is perhaps less certain, since the selenium oxide was used in conjunction with acetic acid-acetic anhydride. If, however, oxidation by selenium dioxide, like peroxidation, involves a radical mechanism, the secondary alcohol represented above as the precursor of the diene might well be a primary product of reaction.

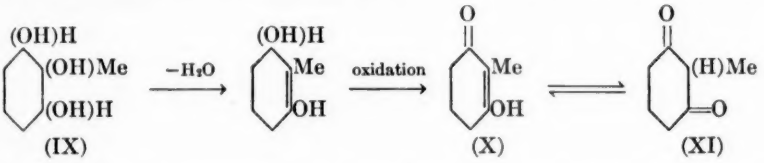
It should be mentioned that dimethylcyclohexene prepared by distillation of the tertiary alcohol (V) in presence of a little iodine, which has been assumed by successive workers to be the pure 1,2-dimethyl-Δ^1-cyclohexene, could conceivably contain substantial amounts of the isomeric Δ^2 compound (VI) as also



a little of the isomeric methylene compound (VII) and, indeed, Lebedev and his coworkers[8] have claimed that rate-of-hydrogenation tests show that the dimethylcyclohexene formed by a variant process, *viz.*, the dehydration of (V) with 30 per cent sulfuric acid, is actually a mixture of all three isomeric olefins. The foregoing demonstration was carried out in the first place with carefully rectified dimethylcyclohexene prepared by the iodine-dehydration method, which at no stage gave indication of containing any significant amount of (VI) or (VII), the former of which by its presence must have invalidated the work. To remove all uncertainty, the demonstration was repeated with a sample of homogeneous dimethylcyclohexene regenerated from the crystalline dibromide (VIII) (which incidentally agreed exactly in physical constants with the iodine-dehydration product) without any important difference accruing in the result.

The opportunity presented by the present investigation has been taken to identify the only secondary derivative of cyclohexene autoöxidation products so far isolated which remained uncorrelated with the general hydroperoxidation scheme developed in previous papers of the series. The compound in question was the crystalline acidic by-product, $C_7H_{10}O_2$, formed by the action of aqueous alkali on (apparently)[9] either 1-methylcyclohexene-3-hydroperoxide or 1,2-dimethylcyclohexene-3-hydroperoxide. The compound, from the monomethyl-hydroperoxide, was reprepared and found to exhibit a characteristic absorption spectrum, that of 2-methylcyclohexan-1,3-dione. This, together with its monoacidity, its crystalline nature, and easy oxidizability by perman-

ganate[10] to give an acid, identified as glutaric acid, leaves no doubt as to its being the methyldihydroresorcinol (X, XI). The formation of the latter cannot easily be accounted for except on the basis of dehydration of the triol (IX) (a major product of the treatment with alkali), followed by oxidation of the



resulting enol to the corresponding dione by active oxygen derived from decomposing ·OOH groups. In the case of the dimethylcyclohexene hydroperoxide, the corresponding triol contains the pinacolic grouping, ·CMe(OH)·CMe(OH)·, which is able to liberate both methyl and hydroxyl groups in the manner characteristic of pinacolones. Of the two possible courses of reaction, *viz.*, to give the pinacolone, R·CMe,CO·R′, or (by elimination of MeOH) the enol, ·CMe:C(OH)·, the latter is found in practice to be preferred.

EXPERIMENTAL

1,2-Dimethylcyclohexene Hydroperoxide.—1,2-Dimethylcyclohexene (75 grams), prepared by the dehydration of 1,2-dimethylcyclohexan-1-ol in the presence of iodine[11], was oxidized at 35° in a quartz flask illuminated by a Hanovia U.V.S. 500 lamp. During 210 minutes oxygen (6 liters) was absorbed. After removal of unchanged hydrocarbon (about 30 grams) and other easily volatile products by gentle heating (bath below 45°) the residue was fractionally distilled at <1 mm. The main peroxide fraction (12.2 grams), distilling at 70–75°/0.5 mm., had $n_D^{18°}$ 1.4908 (Found: C, 68.75; H, 10.1. Calc. for $C_8H_{14}O_2$: C, 67.55, H, 9.9%). It was a colorless oil which (when determined immediately for peroxide by the colorimetric method of Bolland, gave P.O.C. 28.4% (calc. for pure peroxide: P.O.C., 22.2%), but after being kept for 5 days at 0° gave P.O.C. 21.4% by the colorimetric method, but only 14.4% by the potassium iodide method of Dastur and Lea[4]. On refractionation, the main distillate (b. p. 72–74°/0.5 mm.; 11.5 grams) then had C, 69.15; H, 10.15; P.O.C. (colorimetric) 29.7; P.O.C. (potassium iodide method) 17.7%.

Hydrogenation of the Hydroperoxide.—The refractionated hydroperoxide (10.8 grams) was dissolved in absolute alcohol (100 cc.) and hydrogenated in the presence of 0.4 gram of freshly prepared Adams's platinum catalyst. Rapid absorption of 1470 cc. (N.T.P.) of hydrogen occurred, but then no more gas was taken up even after a further 0.4 gram of catalyst had been added and the reaction mixture warmed to 55°. The filtered mixture was distilled; the main (alcoholic) oxidation product (7.2 grams) had b. p. 52°/0.1 mm., $n_D^{16°}$ 1.4790 (Found: C, 74.9; H, 11.6. Calc. for $C_8H_{16}O$: C, 75.0; H, 12.5%), and was, therefore, incompletely saturated. This product was dissolved in pure ethanol (125 cc.) and shaken in hydrogen at 65° with a mixture of 0.4 grams each of Adams's platinum and palladium catalysts. A further slow uptake of hydrogen set in, and continued until saturation was substantially complete. The distilled reduction product consisted mainly of an alcoholic product (5.7 grams) having b. p. 50–54°/0.1 mm., $n_D^{20°}$ 1.4647 (Found: C, 73.75; H, 12.35%).

Composition of Hydrogenation Product.—The almost saturated reduction product (3.4 grams) was heated with a few small crystals of iodine at 180–190°

for 30 minutes and the dehydrated material allowed to distil. The oily distillate (1.8 grams) was well washed with water, dried over calcium chloride, and distilled over sodium. The product was a slightly impure hydrocarbon (1.1 gram) having $n_D^{17°}$ 1.4598 (Found: C, 85.6; H, 12.7. Calc. for C_8H_{14}: C, 87.2; H, 12.8%). This was converted into the corresponding bromo-adduct by dissolving it in pure chloroform (2 cc.) and adding to the solution at 0° bromine (1.8 grams) dissolved in chloroform (2 cc.). The adduct, when worked up, consisted of a mixture of oily and crystalline dibromides; the solid (1.0 gram), after being twice crystallized from dry alcohol, had m. p. 151° and was identified as pure 1,2-dimethyl-Δ^1-cyclohexene dibromide (Found: Br, 59.35. Calc. for $C_8H_{14}Br_2$: Br, 59.35%). Repetition of the bromination, using pure 1,2-dimethylcyclohexene gave an exactly similar result, 1.2 gram of the dibromide being obtained. Thus, the hydrocarbon formed by the dehydration consisted almost wholly of 1,2-dimethyl-Δ^2-cyclohexene.

The portion of the hydrogenation product which remained undehydrated by the iodine treatment gave on distillation an alcohol (0.9 gram) having b. p. 68–72°/12 mm. This alcohol, crude 1,2-dimethylcyclohexan-3-ol, gave, when heated at 110–120° for 30 minutes with α-naphthyl isocyanate (1.3 gram), a crude *urethane* (0.6 gram), m. p. 134–137°, which, after recrystallization from ligroin (b. p. 100–120°), formed colorless prisms, m. p. 141° (Found: C, 76.55; H, 7.6; N, 4.75. $C_{19}H_{23}O_2N$ requires: C, 76.75; H, 7.8; N, 4.7%). The same α-naphthylurethane (m. p. 140°) could also be formed, although in poor yield, from the unfractionated hydrogenation product (Found: C, 76.75; H, 8.0; N, 4.7%); the diminished yield is probably due to some dehydration of the tertiary alcohol by the isocyanate, since Bickel and French[12] have observed that free water has an adverse effect on the reaction of α-naphthyl isocyanate with secondary alcohols. The urethane showed no depression of melting point when mixed with an authentic specimen (below).

Synthesis of 1,2-*Dimethylcyclohexan-3-ol.*—*o*-Xylene (200 grams) was nitrated by the method of Emerson and Smith and converted into 3-nitro-*o*-xylene (118 grams). The latter was converted *via* the corresponding amine (85 grams) and then the iodide (124 grams) into crude 2,3-dimethylphenol (56 grams). The crude phenol melted at 44–47° (Smith and Opie record m. p. 65–66°), but, after several crystallizations from ligroin (b. p. 40–60°) a fraction was isolated having m. p. 71–73° (Short, Stromberg and Wiles,[13] record 73.5–74.5°; Kruber and Schmidt[14], record 75°); the residue doubtless contained isomers of the desired 2,3-dimethylphenol, formed by nitration occurring elsewhere than at the 3-position. Hydrogenation of the compound, m. p. 71–73°, was conducted in ethanol (100 cc.) at 180°/100 atm., using Raney nickel as catalyst, this procedure being more satisfactory than that employed by Sabatier and Mailhe[15] for 3,4-dimethylphenol. The hydrogenation gave a product from which 1,2-*dimethylcyclohexan-3-ol* (13 grams) was isolated by fractional distillation; this had b. p. 77–79°/12 mm. and $n_D^{18°}$ 1.4662 (Found: C, 74.65; H, 12.55. $C_8H_{16}O$ requires C, 75.0; H, 12.5%). The synthetic alcohol (1 gram) gave when heated with α-naphthyl isocyanate (1 gram) at 110–120° for 30 minutes the corresponding urethane, m. p. 130–133° (0.6 gram) which on recrystallization melted at 138–140° (Found: C, 76.65; H, 7.8; N, 4.60%).

Decomposition of 1-*Methyl-*Δ^2*-cyclohexene-5-hydroperoxide with Alkali.*—1-Methylcyclohexene hydroperoxide (12.5 grams), prepared as described by Farmer and Sundralingam[2], was mechanically shaken with 300 cc. of *N* sodium hydroxide. The aqueous product was thoroughly extracted with ether, then

acidified with 6 *N* sulfuric acid, and finally continuously extracted with ether for 7 hours. The dried ether extract gave, on evaporation, an oily liquid containing some suspended crystals, m. p. 196–199°. The latter, recrystallized from 96% alcohol, had m. p. 205–207° (0.2 gram) (Found: C, 66.75; H, 8.2. Calc. for $C_7H_{10}O_2$: C, 66.65; H, 8.0%), the same as that recorded by Butz[16] for 2-methylcyclohexan-1,3-dione. The absorption spectrum of this material, kindly determined for us by H. P. Koch, had the characteristics: max. A., 2620; Σ, 17,000 (0.001 molar solution used). Butz[16] records for methylcyclohexandione: max. 2610 A.; Σ, 17,000 (0.000606 molar solution used).

Purification of 1,2-*Dimethyl*-Δ^1-*cyclohexene.*—The hydrocarbon, prepared as described above by dehydration of 1,2-dimethylcyclohexan-1-ol in presence of a little iodine (95 grams), was dissolved in chloroform (150 cc.) and treated, while cooled in ice-salt, with bromine (138 grams) dissolved in chloroform (150 cc.) during 3½ hours with rapid stirring. The solvent was removed under reduced pressure (below 50°), and the residual mixture of solid and liquid dibromides filtered. The liquid dibromide was not used, but the solid was collected and crystallized several times from dry ethanol, the dissolution on each occasion being conducted with the minimum of heating (owing to the ready interaction of the bromide and alcohol to form ethoxy compounds) and the crystallization each time rapidly promoted by rapidly cooling the solution to −5°. At best, only 85 grams of solid dibromide having m. p. 145–148° together with 17 grams of somewhat impure dibromide (m. p. 140–145°) survived this extremely wasteful crystallization.

The hydrocarbon was regenerated from the pure solid dibromide (97 grams) by dissolving the latter in pure acetone containing a trace of zinc chloride, and debrominating it with zinc. For this purpose, the solution, contained in a flask provided with a gas inlet tube and a reflux condenser, was treated with granulated zinc (50 grams) in portions, the reaction mixture being warmed at the beginning to promote reaction. When ebullition had ceased, the reaction product was cooled, poured into water and the oily hydrocarbon taken up in ether. The ether extract was dried over potassium carbonate and the ether removed through a column; the residual dimethylcyclohexene was twice distilled over sodium in an atmosphere of pure nitrogen, and the product (14.0 grams) had b. p. 134°, and $n_D^{15°}$ 1.4616 (Found: C, 87.1; H, 12.8. Calc. for C_8H_{14}: C, 87.2; H, 12.8%). Dimethylcyclohexene, ordinarily obtained by the iodine dehydration method, has $n_D^{15°}$ 1.4610.

Peroxidation of Pure 1,2-*Dimethyl*-Δ^1-*cyclohexene.*—The pure hydrocarbon obtained by debromination of solid dimethylcyclohexene dibromide was oxidized in U.V. light and the oxidation product rectified and finally hydrogenated all exactly as described above. The behavior throughout, and the products of peroxidation and of hydrogenation agreed so closely with those described for "ordinary" dimethylcyclohexene, that further description is unnecessary. Clearly, both a primary and a tertiary dimethylcyclohexene can be obtained by hydrogenation of the hydroperoxidation product of homogeneous 1,2-dimethylcyclohexene.

RESUMÉ

The peroxidation product obtained by photoöxidation of 1,2-dimethyl-Δ^1-cyclohexene appears to contain both 1,2-dimethyl-Δ^1-cyclohexene-3-hydroperoxide and 1,2-dimethyl-Δ^2-cyclohexene-1-hydroperoxide in accordance with the radical hydroperoxidation hypothesis previously advanced[3], since its

hydrogenation product contains about equal amounts of the corresponding saturated secondary and tertiary alcohols. The crystalline acidic byproduct obtained by the action of alkali on the hydroperoxidation product of either 1-methyl-Δ^1-cyclohexene or 1,2-dimethyl-Δ^1-cyclohexene is the dihydroresorcinol, 2-methylcyclohexan-1,3-dione.

This work forms part of a program of fundamental investigation on rubber undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

[1] Part VII by Farmer, Koch and Sutton, *J. Chem. Soc.* **1943**, p. 541.
[2] Farmer and Sundralingam, *J. Chem. Soc.* **1942**, p. 121.
[3] Bolland, Sundralingam, Sutton and Tristram, *Trans. Inst. Rubber Ind.* **17**, 29 (1941).
[4] Dastur and Lea, *Analyst* **66**, 90 (1941).
[5] The peroxide content is by definition twice the active oxygen content as measured experimentally, so that if more than one atomic proportion of oxygen from each .00. grouping becomes available as active oxygen, the peroxide value found experimentally may considerably exceed the total oxygen content in the compound as determined by elementary analysis. This apparent absurdity is encountered in the present case.
[6] Bodendorff, *Arch. Pharm.* **271**, 1 (1933).
[7] Guillemonat, *Ann. chim.* **11**, 141 (1939).
[8] Lebedev, Kobliansky and Yakubchik, *J. Chem. Soc.* **127**, 417 (1925); Lebedev and Platonov, *J. Chem. Soc.* **1930**, 321.
[9] The formation from either has now been shown with certainty.
[10] Farmer and Sundralingam, *J. Chem. Soc.* **1942**, p. 136, 137.
[11] Signaigo and Cramer, *J. Am. Chem. Soc.* **55**, 3326 (1933).
[12] Bickel and French, *J. Am. Chem. Soc.* **48**, 747 (1926).
[13] Short, Stromberg and Wiles, *J. Chem. Soc.* **1936**, p. 322.
[14] Kruber and Schmidt, *Ber.* **64**, 2274 (1931).
[15] Sabatier and Mailhe, *Compt. rend.* **142**, 553 (1906).
[16] Butz, *J. Org. Chem.* **8**, 515 (1943).

PREPARATION AND PROPERTIES OF RUBBERLIKE HIGH POLYMERS. I. POLYMERIZATION OF DIENES AND VINYL COMPOUNDS IN BULK *

C. KONINGSBERGER AND G. SALOMON

RUBBER FOUNDATION, DELFT, NETHERLANDS

INTRODUCTION

Since plastics and synthetic rubbers have become available on an industrial scale, the general nature of elasticity of long-chain molecules has been discussed in a great number of papers. Very little is known, however, about the exact conditions under which such polymers can be prepared on a laboratory scale for comparative measurements. To fill this gap, experiments were started before the war.

As is now well known, a synthetic rubber must not be considered as a chemical compound of definite structure, but as a mixture of macromolecules which differ in size, in arrangement of the elementary units, and in regularity of macromolecular pattern. The physical, chemical, and technological properties of a synthetic rubber depend on the composition of this mixture and on the nature of the molecular units from which the rubber is built up. To compare synthetic rubbers and plastics with natural rubber and its derivatives, we prepared a number of polymers (under reproducible conditions) of gradually increasing complexity. In this paper we shall treat the bulk polymerization of a single component; in the next one we shall deal with the bulk polymerization of mixtures; and, finally, we shall discuss copolymerization in emulsion. The comparison of the chemical, physical, and mechanical properties of these polymers will be discussed in further communications of this series.

Starting with a vinyl compound, one obtains polymers which may be considered as substituted paraffins. In most cases the products, isolated after short reaction times (*e.g.*, at a yield of 5 per cent) do not differ essentially from those isolated after long reaction times (*e.g.*, at a yield of 95 per cent). In that case a precise reproduction of the reaction time is not of primary importance. But polymers from dienes are very reactive olefins, which may change their properties during the course of polymerization. The following side reactions may be expected gradually to modify the properties of the polymer originally formed: (1) cyclization within the macromolecules; (2) cross-linking between macromolecules; (3) addition of the diene to a double bond of the polymer in a Diels-Alder reaction; and (4) formation of a dimer and addition of the dimer to the polymer. It is, therefore, evident that in the case of dienes a precise knowledge of the time-yield relation is of fundamental importance for reproducible results.

As the rate of the chain reactions depends on the presence of minute quantities of impurities, the definition of the purity of the starting material by the

* Reprinted from the *Journal of Polymer Science*, Vol. 1, No. 3, pages 200–216, May 1946. This paper is Communication No. 53 of the Rubber Foundation.

application of classical chemical and physical methods must be supplemented by a determination of the catalytic purity. We have found that heat polymerization itself is the most convenient method to test this property of a diene. It is very unlikely that, at 100° C, any uncatalyzed heat polymerization of the ordinary dienes and vinyl compounds takes place. The rate of the apparent heat polymerization is, therefore, determined by traces of oxidation products of the olefin, which act as catalyzers.

2,3-Dimethylbutadiene is somewhat troublesome to prepare, but convenient to purify, and our blank polymerization experiments with the pure diene led to satisfactorily reproducible results. Butadiene, on the other hand, can be prepared readily, but is somewhat more difficult to purify. Polymerization was carried out with samples containing 8 per cent gaseous hydrocarbon impurities; nevertheless very similar yields were obtained in duplicated experiments. Isoprene has neither advantage of the two other dienes: it is difficult to prepare in satisfactory yields, and troublesome to handle and to free from the many impurities which originate in the starting material, dipentene. Only a few experiments with this compound were carried out for comparative purposes.

The present paper describes the results of the polymerization of the pure dienes (compared with dienes to which definite amounts of catalyst have been added) and similar experiments with styrene and acrylonitrile, and compares the kinetic results, as well as the properties of the polymers.

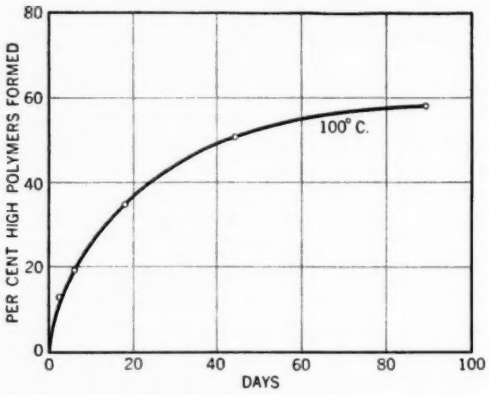


FIG. 1.—Heat polymerization of dimethylbutadiene at 100° C.

POLYMERIZATION OF DIENES

2,3-Dimethylbutadiene.—The samples used were of the desired analytical purity and contained about 0.08 per cent formaldehyde and 0.05 per cent labile peroxides. The effect of these impurities on the stability at 100° C is illustrated in Figure 1.

Our ultimate yield of polymer did not exceed 60 per cent. Whitby and Gallay[1] found 46 per cent polymer after 30 days at 100° C, which corresponds to our value.

Heat polymerization is accompanied by the dimerization (Diels-Alder reaction) of the diene. According to Whitby and Gallay, all of the remaining diene had been transformed to the dimer after 30 days. Dimerization has

been studied by Kogerman[2], and from his results it is evident that dimerization becomes prevalent at higher temperatures; Figure 2 gives an example for 150° C.

As the rate of dimerization is probably not sensitive to polymerization catalysts, Kogerman, who was interested only in the former reaction, used a dimethylbutadiene of lesser catalytic purity (see Figure 3). The actual effect of dimerization is still more important at 150° C than would appear from Figure 2. Kogerman found also a very large temperature function for the dimerization, but only a small one for the polymerization. The latter fact is also illustrated by our results (Figure 3).

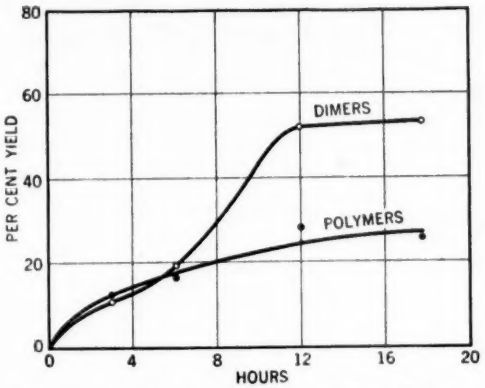


FIG. 2.—Rate of dimerization and polymerization of dimethylbutadiene at 150° C (after Kogerman).

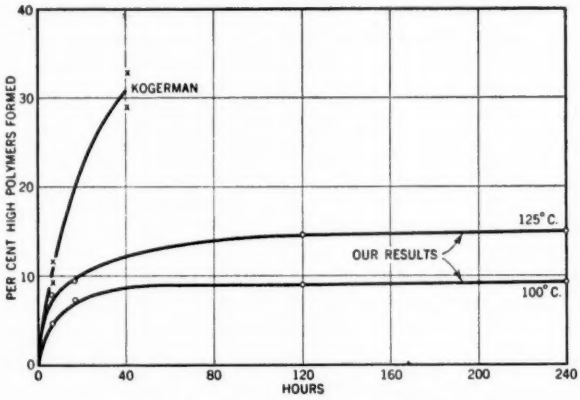


FIG. 3.—Rate of heat polymerization at 100° and 125° C.

Our reactions start at a rate which should yield about 100 per cent of polymer within two days, but after the formation of the first small fraction, the rate decreases by a factor of ten. This decrease continues gradually as the traces of catalysts are used up. From Figure 1 it appears that, even after three months, no more than about 58 per cent of polymer has been formed at 100° C.

It is evident from these results that a catalyst should be used which is sufficiently active to polymerize all the material within a few days at 100° C; otherwise considerable loss of monomer is caused by dimerization.

The effect of benzoyl peroxide was much less apparent than in the well-known case of styrene. The influence of 0.1 per cent benzoyl peroxide was negligible, because the systems already contained a larger amount of labile peroxides as an impurity. High yields were obtained with 1 per cent benzoyl peroxide, but only after ten days. The reaction products were strongly oxidized and sticky, and it was evident that this would not be a convenient laboratory method for the preparation of a rubber.

Buizov[3] was the first to describe the catalytic effect of diazoaminobenzene, and his results have been confirmed by other Russian authors. As may be seen from Figure 5, it is indeed a powerful catalyst for dimethylbutadiene polymerization. The reaction is accelerated continuously, so that more than 95 per cent of the material is polymerized after two days at 125° C and after a week at 100° C. Even at 70° C, the reaction proceeds smoothly and products of excellent quality can be isolated after three months.

Schulz has studied in great detail the action of free radicals as polymerization catalysts[4]. Compounds like diazoaminobenzene apparently disintegrate slowly while producing free radicals. The shape of the curves (Figure 5) is in agreement with this assumption. A certain amount of radicals is produced continuously, catalyzing the reaction until polymerization is completed. The course of the reaction is, therefore, more regular and more easily reproducible than with benzoyl peroxide. The latter catalyst obviously decomposes, losing its activity long before polymerization has been completed.

The powerful influence of this catalyst is also illustrated by a series of experiments with increasing concentrations (Figure 6). As little as 0.1 per cent diazoaminobenzene is sufficient to produce more than 90 per cent polymer. The catalytic effect is approximately proportional to the square root of the concentration, a typical phenomenon for catalysis induced by radicals and previously discussed by Schulz. Our figures are very reproducible and such factors as the quality of the glass of the test tubes do not influence the reaction rate. When working with larger quantities, *e.g.*, batches of 100 grams, kept in a hot air oven, somewhat shorter reaction times are found, probably through insufficient dissipation of heat during the reaction.

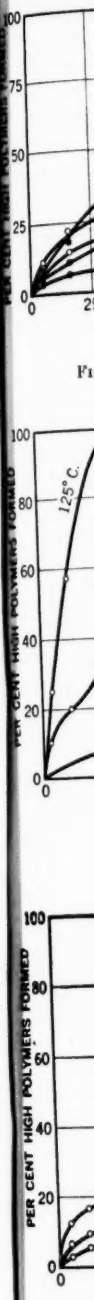
The rate of diazoaminobenzene-catalyzed polymerization shows a temperature dependence of 2.5 for every 10° rise between 70° and 100° C, and 1.8 for every 10° rise between 100° and 125° C. The slow thermal decomposition of the azo compound may be the rate-determining factor at lower temperatures.

Buizov assumed that the capacity to occur in tautomeric forms determined the catalytic properties of a compound. Since neither the ethyl ester of benzoylacetic acid nor phenyl isothiocyanate has any catalytic effect, this hypothesis may be dismissed. Curiously enough, a combination of these compounds with diazoaminobenzene increases the effect of the latter somewhat.

Glacial acetic acid[5] has no measurable accelerating effect on the polymerization of dimethylbutadiene under our experimental conditions. Piperidine[2] has a measurable retarding effect at 100° C.

Diazoaminobenzene is also a powerful vulcanizing agent[6], but other vulcanizers such as *m*-di-nitrobenzene, chloranil, and nitrophenol, have no essential catalytic influence on bulk polymerization of dimethylbutadiene.

The only active compound which is even superior to diazoaminobenzene is *p*-tolyldiazoaminobenzene. From this positive result and the negative experiments (see above) we conclude that the reproducible formation of rubberlike high polymers from dienes can be catalyzed by free radicals from diazo compounds. A new field may be opened by this conclusion, since different com-



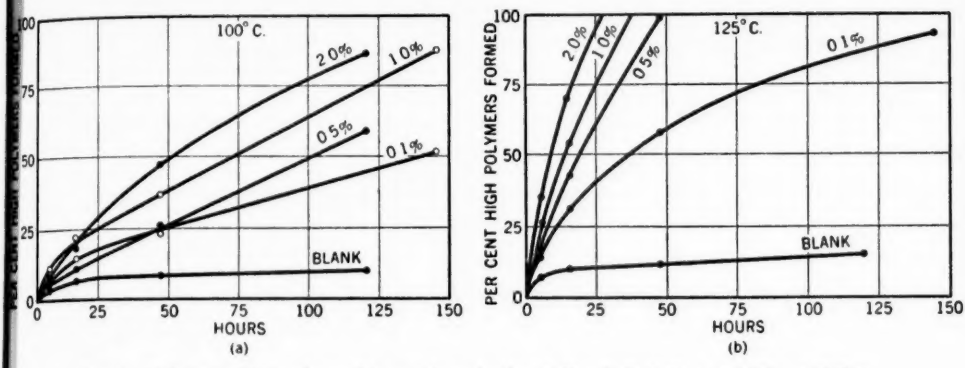


FIG. 4.—Influence of benzoyl peroxide on polymerization of dimethylbutadiene at 100° and 125° C.

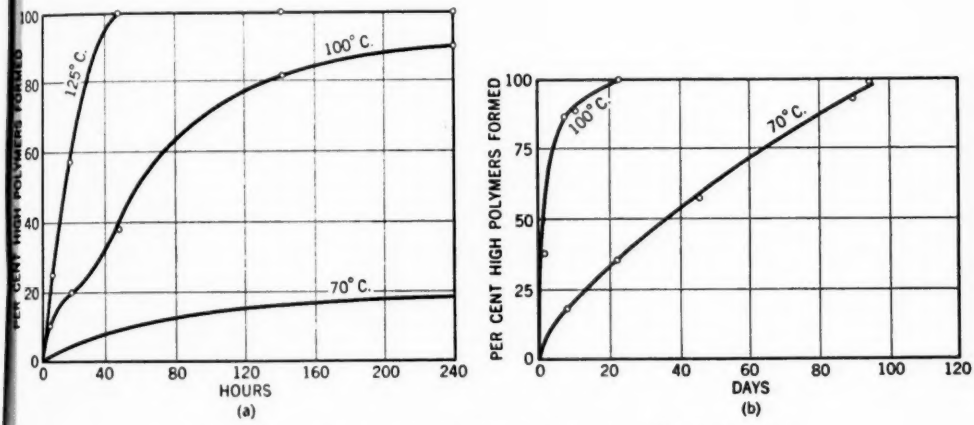


FIG. 5.—Catalytic effect of 1 per cent diazoaminobenzene on dimethylbutadiene.

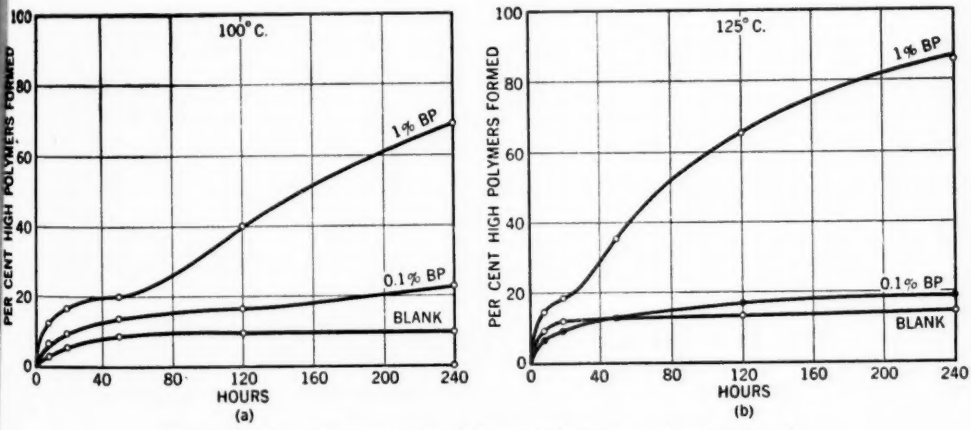


FIG. 6.—Influence of concentration of diazoaminobenzene on polymerization of dimethylbutadiene at 100° and 125° C.

binations of radical sources and inhibitors could lead to products of varying molecular size and shape.

Since diazoaminobenzene is a powerful vulcanizer, one might expect a strongly cross-linked polymer; this, however, is not the case. The vulcanizing action occurs only at 150° C, with decomposition of the catalyst, and obviously has no direct bearing on its catalytic activity at lower temperatures.

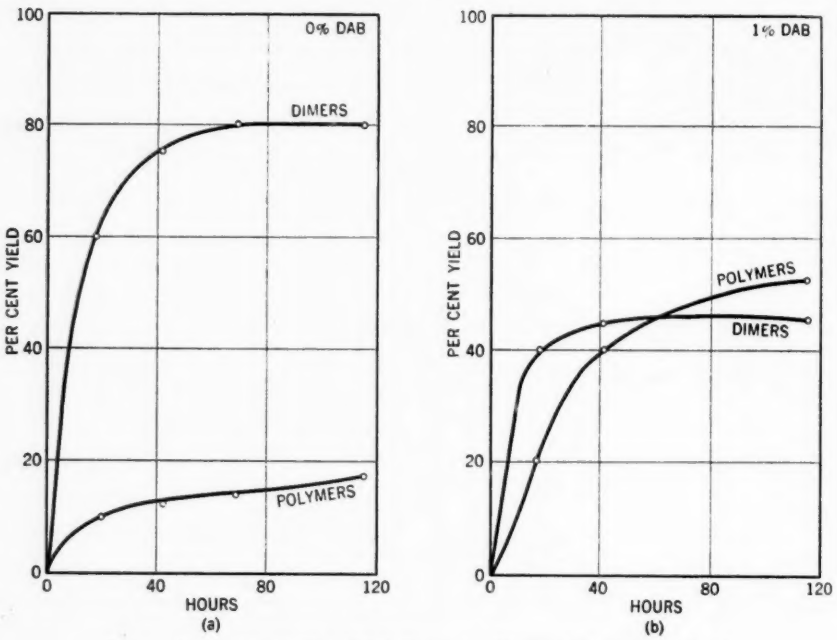


FIG. 7.—Heat polymerization of butadiene (a). Diazoaminobenzene-catalyzed polymerization of butadiene (b). Experiments at 125° C.

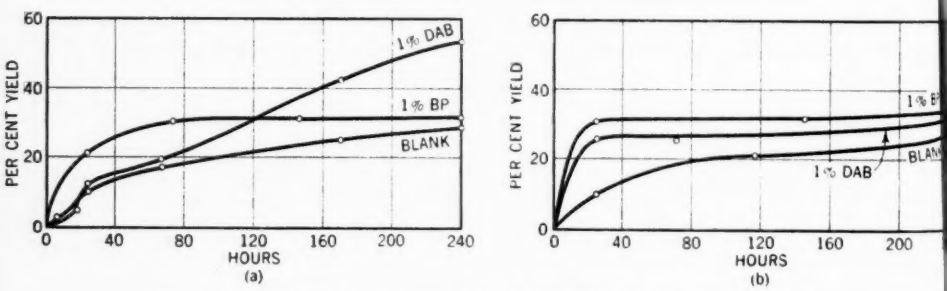


FIG. 8.—Formation of high polymers (a) and dimers (b) from butadiene at 100° C, with and without catalysts.

The molecular size and form change with polymerization time. Up to about 80 per cent yield, nearly all of the polymer is soluble in the usual rubber solvents, but heating the polymer for another ten days under catalytic conditions at 100° C makes it insoluble. A benzene solution of the soluble fraction shows a marked increase in relative viscosity with increased polymerization time. All these differences are, however, not larger than those between

natural rubbers of varying plasticity, and are easily minimized by vulcanization (see Part IV of this series of communications).

The decomposition products of diazoaminobenzene act as antioxidants and, because they are difficult to extract completely, and because, moreover, no peroxides are used for polymerization, the resulting methyl rubber has much better aging qualities than a product prepared by heat or cold polymerization. It should, however, be borne in mind that the thermal stability of these polymeric hydrocarbons is lower than that of natural rubber. The mechanical

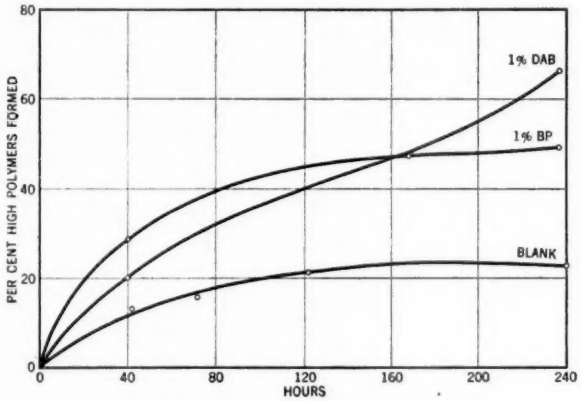


FIG. 9.—Heat polymerization and effect of catalysts on polymerization of isoprene at 100° C.

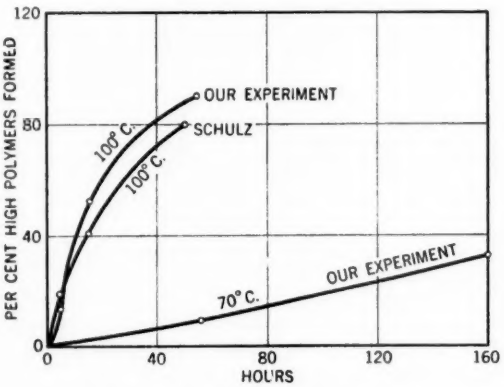


FIG. 10.—Heat polymerization of styrene.

properties will be discussed more fully later; the outstanding difference from natural rubber is that the limiting temperature for rubberlike properties is considerably higher.

Butadiene.—The product was prepared from cyclohexene, the resulting mixture having about the following composition: butadiene, 92.3; propene + butene, 4.4; and butane + pentane, 3.3 per cent.

As some of the monoölefins may have copolymerized, yield determinations are uncertain within 5 per cent. On the other hand, separation of the starting

material, dimers, and polymers was particularly easy to carry out, making it possible to determine the ratio of dimers to polymers fairly accurately.

As may be seen from Figures 7 and 8, dimerization is the main reaction at 100° and 125° C. Russian authors found a ratio of dimers to polymers of 6–9 at these temperatures[7], while our results show a ratio of 1 at 100° C and about 5 at 125° C, indicating that our samples of butadiene had a greater tendency to polymerize. They probably also contained more peroxides, which fact is borne out by the slight effect of a further addition of 1 per cent benzoyl peroxide. As may be seen from Figure 8, the influence of benzoyl peroxide is negligible. The catalytic effect of diazoaminobenzene on butadiene is about the same as on

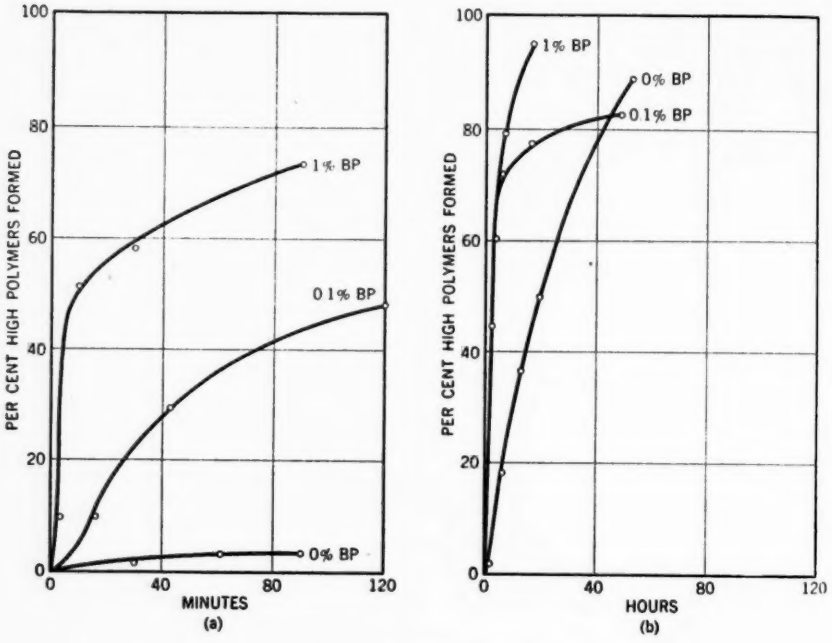


FIG. 11.—Peroxide-catalyzed polymerization of styrene at 100° C.

dimethylbutadiene, so that the faster dimerization of the first compound cannot be suppressed completely (see Figure 8). Perhaps other sources of radicals will prove to be more effective.

Butadiene has already been polymerized with diazoaminobenzene by Russian investigators[18], and comparison with their results shows that purity of the starting material influences both reaction time and ultimate yield.

Labile peroxides will react with the radicals produced by diazoaminobenzene and the impurities of butadiene can, therefore, interfere with the activity of the catalyst, as is shown by the data in Table I.

As the dimerization of butadiene shows an activation energy of 24 kcal. per mole, it is obvious that the rate of dimerization will be much smaller at lower temperatures. As it is possible to start polymerization at lower temperatures, *e.g.*, by the use of sodium or by peroxide catalysts in emulsion, higher yields

TABLE I

INFLUENCE OF PURITY ON YIELDS OF POLYBUTADIENE AT 100° C

Source of butadiene	Per cent Diazoamino-benzene	Reaction time, hrs.	Per cent yield	Authors
Gasoline hydrocarbons	0.44–1.1	170–816	10–40	Balandina *et al.*
Alcohol	0.88	562	38	Balandina *et al.*
Cyclohexene	1.25	116	50	Koningsberger and
	1.25	340	60	Salomon

of polybutadiene can be obtained. This is one of the decisive factors which finally led to the industrial application of polymerization in emulsion.

The properties of polybutadienes change very distinctly with the reaction time. Young polymers are soft, plastic, and partly soluble. Old polymers, particularly those which have been kept under the influence of the catalyst

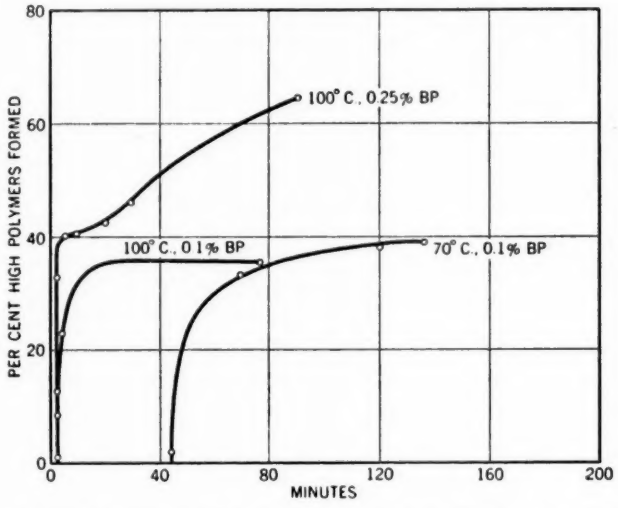


FIG. 12.—Influence of small quantities of benzoyl peroxide on polymerization of acrylonitrile.

after the reaction has been completed, are only highly elastic in the swollen state; the dimer acts as a swelling agent, but after drying they are brittle and completely insoluble.

The old polymers swell in benzene to about 2500–3000 per cent, which indicates a cross-linking comparable with the state of a slightly vulcanized rubber. The mechanical properties are, however, quite different, and show the shortcomings which are encountered to a lesser degree with Buna-S.

Our polybutadienes aged in the same way as Buna-S, *i.e.*, becoming hard and brittle. We may learn from these results that the essential difference between natural rubber and Buna-S is not caused by mixed polymerization, but by a different structure of the polymeric diene.

Isoprene.—The results of a few experiments we have carried out are reported in Figure 9, and are in agreement with our anticipations. The action of catalysts is about the same as with butadiene. Dimerization is distinctly greater

than with dimethylbutadiene, but less than with butadiene. Yields of polymers can probably be improved by evaluation of optimum catalytic conditions.

These polymers change from being tacky and very soft to being elastic but still soft. They are difficult to free completely from dimers (terpenes) and,

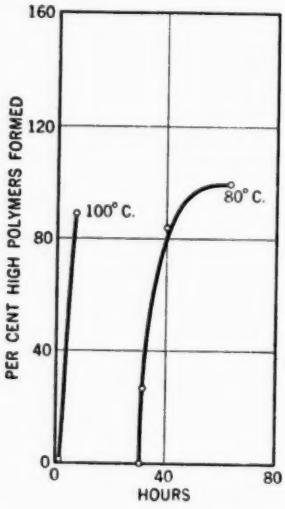


FIG. 13.—Influence of 1 per cent diazoaminobenzene on polymerization of acrylonitrile.

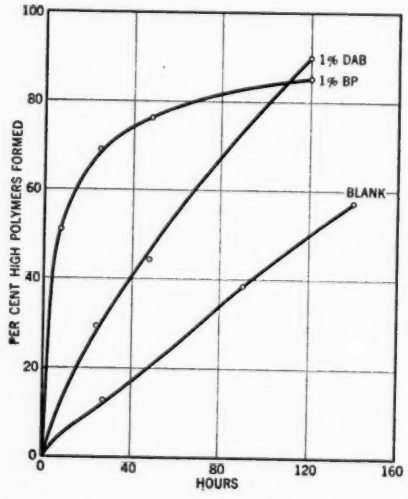


FIG. 14.—Polymerization of styrene (3 parts) dissolved in toluene (7 parts) at 100° C.

as the latter strongly induce autoöxidation, the polymers deteriorate quickly, becoming sticky. It should be emphasized that these polymers are fundamentally different from polybutadiene, and are more closely related to methyl rubber and natural rubber.

POLYMERIZATION OF VINYL COMPOUNDS

Styrene and acrylonitrile are components of Buna-S and Perbunan. Styrene has been studied extensively by many authors, and we shall discuss only a few facts which are important for the understanding of copolymerization. Little has been published about acrylonitrile and our experiments may, therefore, broaden existing concepts about the properties of this interesting compound.

Styrene.—Cuthbertson, Gee, and Rideal[9] have proved that pure styrene is a stable compound. The olefin is extremely autoöxidizable and contains 0.01–0.03 per cent labile peroxides and traces of aldehydes. The rate of the heat polymerization of our starting material was practically identical with that found by Schulz and Husemann[10].

The effect of benzoyl peroxide is much more pronounced at the beginning of the reaction than during its course. This indicates that the catalyst is quickly decomposed, and most of it is used up long before all of the starting material has been polymerized.

Diazoaminobenzene also acts as a catalyst; the effects compared with heat polymerization are, however, small under our experimental conditions.

The polymers from styrene were soluble in the usual solvents, which proves that the starting material was free from divinylbenzene[11].

Acrylonitrile.—The outstanding property of this olefinic compound is its complete thermal stability even at 150° C. This is readily explained by the lack of autoöxidation. Even after standing in the presence of air for a long time, the pure liquid is free from traces of peroxides. The addition of minute quantities of peroxides causes a vigorous reaction. As the polymers are completely insoluble in the monomer, the beginning of the reaction may be clearly observed by the occurrence of turbidity.

In the presence of 0.1–0.25 per cent benzoyl peroxide an induction period of two minutes is observed; the reaction then starts explosively, and after a short time, most of the catalyst being used up, comes to a standstill. The induction period is very long at 70° C, but the course of the reaction is about the same as at 100° C. With 1 per cent benzoyl peroxide added, macroscopic explosions occur frequently, even at 50° C. If the sealed glass tube survives, a typical clattering noise, lasting a few seconds, can be heard.

The action of diazoaminobenzene is also marked by a long induction period. The course of the reaction is less violent, since the actual concentration of the free radicals is very small.

The polymers are hard powders, insoluble in organic solvents, with little tendency to swell. They dissolve in solutions of certain salts, *e.g.*, lithium bromide, sodium thiocyanate, and zinc chloride[12]. This proves that they have the same long-chain structure as other polyvinyl compounds; they are not cross-lined. The failure to swell in organic liquids is caused by the exceptionally strong dipole interaction of the nitrile groups. Otherwise equal effects are only encountered with organic polymers containing hydrogen bonds. In methyl acrylonitrile the CN group is partly screened by the CH_3 group and cannot interact to the same extent. The polymers of this compound are, therefore, soluble and strongly swelling in suitable organic liquids. Our observations are in agreement with the results of Kern and Fernow[13].

Polymerization in Solution.—The action of a diene in a mixture with a vinyl compound is, in the simplest case, that of a diluent for the vinyl compound. To get some idea about the course of polymerization in solution we

followed it with toluene as a neutral solvent. The mixture of 3 parts of vinyl compound and 7 parts of toluene is comparable to a typical mixture for the copolymerization leading to Buna-S and Perbunan.

The heat polymerization and that catalyzed by 1 per cent diazoaminobenzene is retarded by a factor of 6–8, indicating somewhat more than a dilution effect. The activity of benzoyl peroxide, on the other hand, is much more reduced.

Acrylonitrile is not quite stable in solution; the solvent, however, was not catalytically pure. One per cent benzoyl peroxide causes nearly as violent a reaction as with the undiluted nitrile, the catalyst being decomposed before all the monomer has been used up. We learn from Figure 15 that an induction period is found again for the action of 1 per cent diazoaminobenzene, which proved to be a fairly effective catalyst.

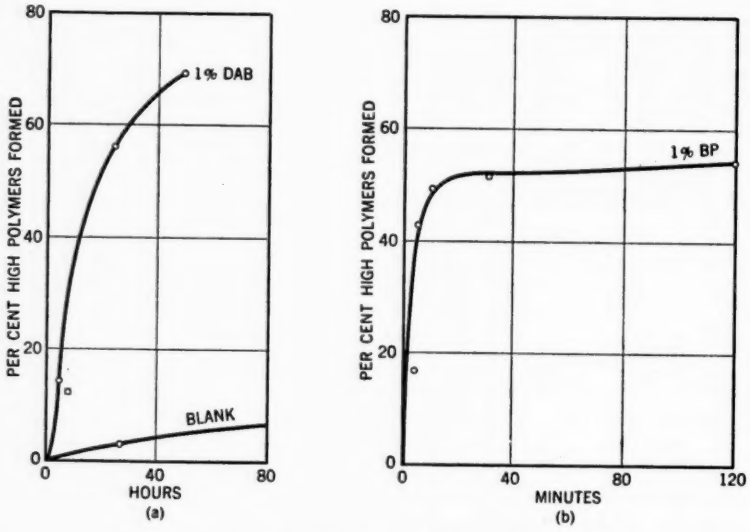


FIG. 15.—Influence of catalysts on polymerization of acrylonitrile dissolved in toluene (3:7) at 100° C.

DISCUSSION OF RESULTS

Kinetics of Polymerization and Dimerization.—Our experiments with the five unsaturated compounds reveal great differences in the rates of polymerization and we will now try to determine the causes of such variations by evaluating possible changes in the factors which determine the rate.

Inhibitors.—Since, in principle, every olefin can react with oxygen, we may expect two possible effects in peroxide-catalyzed polymerization:

1. The polymer is a compound that is not affected by oxygen. In this case polymerization is either promoted or hampered by autoöxidation reactions of the monomer, which can eventually act as an inhibitor.

2. The polymer is a compound that is as reactive toward oxygen as is the monomer. In this case polymerization may be either promoted or hampered by autoöxidation reactions of both polymer and monomer.

Polystyrene is completely stable toward oxygen, and does not react with the catalyst. With dienes the situation is fundamentally different: the polymers are at least as reactive toward oxygen as the diene, and its dimer and most of the labile peroxides originally formed are finally used up by oxidation. Since, moreover, some of the oxidation products are rapidly formed in the macromolecule, small quantities of peroxides become ineffective after a short polymerization time and large quantities are, for the same reason, only moderately active compared with their action on vinyl compounds.

Catalysts.—Although the kinetic effect of the decomposition products from benzoyl peroxide and diazoaminobenzene is very similar, the rate of thermal decomposition is very different for both compounds. Diazoaminobenzene decomposes very slowly at 100° C, so a small but continuous concentration of radicals is produced. Benzoyl peroxide, on the other hand, decomposes violently and autocatalytically in the presence of dienes.

We shall now apply this line of thought to a comparison of reaction times (see Table II).

TABLE II

COMPARISON OF YIELDS AND REACTION TIMES AT 100° C

		Reaction time (hours)						
Catalytic condition	Percentage yield	Dimethylbutadiene	Isoprene	Butadiene	Styrene	Styrene[a]	Acrylonitrile	Acrylonitrile[a]
Natural impurities	5	5	10	4	2	6	~	60
1% benzoyl peroxide	25[b]	60	60	40	0.03	2	0.0005	0.03
1% diazoaminobenzene	25[b]	25	28	25	8	25	1	6

[a] 30 parts of monomer dissolved in 70 parts of toluene.
[b] Calculated by taking the polymers ultimately formed = 100 per cent.

The rate of heat polymerization is not much different for dienes and styrenes, the ratio being 1:3. In the presence of 1 per cent benzoyl peroxide, however, the proportions become:

$$\text{dienes:styrene:acrylonitrile} = 1:500:100{,}000$$

whereas in the presence of 1 per cent diazoaminobenzene the corresponding ratios are only $1:3:\sim 25$.

The solvent toluene, which is susceptible to autoöxidation, has an inhibitory effect on the peroxide catalysis, retarding the reaction about 70 times, while diazoaminobenzene catalysis is retarded only 3–6 times by the same solvent.

Since it is known that the peroxide-catalyzed polymerization of dienes readily takes place in emulsions at much lower temperatures, the results above may be explained by assuming that autoöxidation of dienes and polymers becomes preponderant in homogeneous systems at 100° C.

The mechanism of diazoaminobenzene action is probably the same on the five olefins, and only an increase in olefinic reactivity, in the order of increased polarity of the monomer, becomes evident. High yields of methyl rubber are produced with this catalyst, because its activity remains essentially unchanged until all material has been polymerized. Although the catalytic effect of diazoaminobenzene on butadiene is about the same, only much lower yields of polymers are obtainable, because the rate of dimerization increases in the order: dimethylbutadiene < isoprene < butadiene. Because the dimerization of dimethylbutadiene at 150° C is comparable with that of butadiene at

100° C it is assumed that the energy of activation for the reaction of the latter must be much smaller.

Properties of Polymers and Dienes.—The smooth course of the diazoaminobenzene-catalyzed reactions results in reproducibility of yield and of physical and mechanical properties of the polymers. It has already been stated that methyl rubber differs distinctly from polybutadiene and, combining our results with facts known from the literature, we can distinguish between two types of rubberlike polymers:

GROUP A.—Soft, more or less soluble, the insoluble fraction swelling strongly, and the polymer softening with aging. To this group belong: (1) natural rubber, (2) sodium-polymerized rubber from the three dienes; (3) radical-polymerized rubber from dimethylbutadiene and isoprene, and (4) radical-polymerized rubber from butadiene isolated after a yield of 1–10 per cent. These polymers may differ very much in structure, but only the mechanical strength and the limiting temperature of elasticity are influenced visibly by this fact.

GROUP B.—Hard, insoluble, swelling to about 1500 per cent, with a strong tendency to become brittle, and hardening with aging. To this group belongs polybutadiene, polymerized by action of peroxide or diazoaminobenzene and isolated at yields higher than 20 per cent. It follows from this that the mechanical and chemical properties of polybutadiene can be modified much more by experimental conditions than those of polymers from dimethylbutadiene and isoprene produced under comparable conditions.

EXPERIMENTAL

2,3-Dimethyl-1,3-butadiene.—Starting from acetone, we first prepared pinacol hydrate, according to the method described by Gilman[14]. This substance was then carefully freed from water by fractional distillation and the anhydrous pinacol afterwards purified by simple distillation from an oil bath (*b.p.* 175–176° C at atmospheric pressure). *Yield:* 40 per cent, calculated on the magnesium used.

The conversion of anhydrous pinacol into dimethylbutadiene was carried out in several ways. The best results were obtained by using aniline hydrobromide as a dehydration catalyst[15]. The pinacol was mixed with 1–2 per cent of the catalyst and heated in an oil bath at about 150° C. Decomposition took place in a slow and regular manner; the vapors passed a Widmer column, at the top of which a temperature of about 90° C was maintained by regulating the temperature of the oil bath. The reaction products were condensed and collected in an ice-cooled receiver, in which they separated into two layers. The lower layer, consisting mainly of water, was discarded, and the upper layer, containing the desired product, was first dried over anhydrous calcium chloride and then fractionated. The first fraction, distilling between 65° and 80° C, was the largest of all and contained practically all of the dimethylbutadiene, still in an impure state. The remaining fractions (80–90° C, and 90–100° C, respectively) and a residue (*b.p.* > 100° C) contained mainly pinacolone (formed as a byproduct from pinacol by the pinacolone rearrangement) and some dimer of the diene.

By rectifying the main fraction several times, followed by a double distillation from sodium wire in a stream of dry nitrogen, we finally obtained the hydrocarbon in a very pure state. Average yield: 60 per cent, calculated on pinacol. $B.p._{760}$, 69.0° C; n_D^{20}, 1.4390. According to the literature[16]: $b.p._{760}$,

68.9° C; n_D^{20}, 1.4386. Elementary analysis gave results which were in good agreement with the values expected (C = 87.8 per cent; H = 12.2 per cent).

Determination of active oxygen was carried out by means of a comparative colorimetric method, based on the formation of ferric thiocyanate from ferrous salts[17]. Average results: 0.05 per cent. Traces of aldehyde were also determined colorimetrically by comparison with solutions of known aldehyde content, using Schiff's reagent[18]. Average results: 0.08 per cent, calculated as formaldehyde.

1,3-Butadiene.—This substance was prepared according to Hershberg and Ruhoff[19] from cyclohexene. The method proved to be very satisfactory for laboratory use. The raw product was purified by distillation from bulb to bulb. Average yield: 78 per cent. $B.p._{760}$, −4° C (experimental); −2.6° to −5° C (according to the literature[20]). A modified Podbielniak analysis of a sample of the gas[21] gave the following results:

Butadiene	92.3
Butenes (α and β)	1.5
Propene	2.9
n-Butane	2.4
Pentane	0.9
	100.0

Isoprene.—We used a product obtained by cracking of dipentene[22] and purified by fractional distillation ($b.p._{760}$, 33.5–35° C). It certainly contained still lower boiling impurities, as can be seen from the refractive index; n_D^{20}, 1.4197 (experimental); 1.4216 (according to the literature[23]). Active oxygen: 0.03 per cent; formaldehyde: 0.05–0.1 per cent.

Styrene.—Commercial samples from various sources were used. Those from Eastman Kodak, Fraenkel-Landau, and I. G. Farbenindustrie were of about equal purity, and contained quinol as a stabilizer. They were practically free from dissolved polymer and possessed the correct analytical composition: n_D^{20}, 1.5460 (experimental); 1.5462 (according to the literature[24]). Active oxygen: 0.01–0.03 per cent; formaldehyde: 0.00–0.10 per cent. Before carrying out polymerization experiments, we removed the quinol by shaking with dilute alkali, washing with distilled water, and drying over calcium chloride.

A sample from Usines du Rhône (Poulenc Frères) contained many impurities, among them 2–3 per cent dissolved polymer. In carrying out polymerization experiments by heat alone, it also behaved differently from samples from the above sources.

Acrylonitrile.—Starting from ethylene chlorohydrin, we first prepared the corresponding cyanohydrin. Best results were obtained by the method of van der Burg[25]. The product was purified by distillation *in vacuo*. $B.p._{.4}$: 89° C. Yield: 75 per cent.

Several methods were tried for the conversion of the cyanohydrin into acrylonitrile. The most convenient method appeared to involve the use of sodium acid sulfate as a dehydration catalyst[26]. For laboratory use, the following procedure was employed.

In a round-bottomed flask of 100 cc. capacity, fitted with a short, but effective, column and a graduated funnel, 1 gram of sodium acid sulfate and 20 cc. of ethylene cyanohydrin are placed. This mixture is heated in a metal bath to about 250° C; the reaction proceeds very slowly at first, but afterwards the conversion is accelerated, and it is necessary to lower the temperature of the metal bath to about 230° C. The reaction products, acrylonitrile and

water, pass through the sodium, at the top of which a temperature between 80° and 95° C should be maintained. The vapors are condensed and collected in a graduated tube.

More ethylene cyanohydrin is added dropwise from the funnel to the reaction mixture to compensate for the water and acrylonitrile which are distilled away. In this manner we were able to prepare large quantities of the nitrile from 1 gram of sodium acid sulfate. Even if we had to interrupt our work, we could often use the residue in the flask the next time. It was surprising that in this case the reaction always proceeded more quickly from the beginning, and the yields were better. We can explain this by assuming that there must be formed first an intermediate compound of ethylene cyanohydrin and the catalyst:

The intermediate is then decomposed, yielding acrylonitrile and sodium acid sulfate. Therefore, if we reuse the residue in the flask, which already contains the intermediate compound, we can expect a rapid and more complete reaction.

The distillate, consisting of two layers, is treated with a small amount of sodium sulfate to salt out the nitrile, which is partly soluble in water. The crude product is then separated from the water layer, washed successively with dilute sulfuric acid, dilute caustic soda, saturated sodium sulfate solution, and finally dried over ignited potassium carbonate. The acrylonitrile is then fractionated. Average yield: about 65 per cent. Physical constants (experimental): $b.p._{760}$, 77° C; n_D^{20}, 1.3915. According to other recent investigations[27] they are: $b.p._{760}$, 77.3° C; n_D^{20}, 1.3911. (This set of values is in good accordance with out own data.) Aldehyde content: 0.05 per cent (average). Active oxygen: 0.00 per cent, even after prolonged exposure to air.

The nitrile is not miscible with high-boiling kerosene at room temperature, and with gasoline and pure aliphatic hydrocarbons at somewhat lower temperatures. At 22° C, water dissolves 10.7 per cent by volume (8.7 per cent by weight) of the nitrile; the latter dissolves 2.8 per cent by volume (3.5 per cent by weight) of water at the same temperature. Above 130° C, complete miscibility is observed.

Diazoaminobenzene.—A commercial product was used. After recrystallization, its catalytic activity did not change. Any impurities present, therefore, have no influence on its behavior as a catalyst.

Benzoyl Peroxide.—The commercial product usually contains about 25 per cent water. This was removed by dissolving the substance in chloroform and pouring the solution into an excess of methanol. The peroxide was then precipitated in a pure state, free from moisture.

POLYMERIZATION

For kinetic experiments, 5–10 cc. of the monomers were heated in sealed test-tubes. The tubes were kept in a bath of high-boiling liquid in a thermoregulated stove. Special precautions were taken to make the time of heating as short as possible. For preparative purposes sealed tubes with an intake of 50–100 grams of the monomers were used.

Although the influence of the glass wall on the rate of polymerization of styrene is well known, we found no difference caused by using different kinds

of glass with dimethylbutadiene. This result is plausible, because dienes proved in general to be less sensitive to traces of additional peroxide catalysts.

Polymers were isolated by precipitation with methanol and treated with quinol or phenyl-β-naphthylamine as antioxidants. In the case of butadiene, starting material, dimers, and polymers were separated by fractional distillation.

A few of the preparative experiments may serve as examples:

Methyl Rubber.—Standard method: 72 grams of dimethylbutadiene and 0.72 gram of diazoaminobenzene were heated for a certain period; the polymer was extracted with methanol for 18 hours in the presence of an antioxidant, carefully dried on a mill, weighed, and analyzed. Solubility in benzene was determined before drying on a mill.

Temperature (° C)	Time (hours)	Yield (grams)	Yield (percentage)	Solubility in benzene (percentage)	Percentage C (calc. 87.8)	Percentage H (calc. 12.2)	Residue, 100% − (C + H)
100	96	64	88	5–10	86.7	11.5	1.8
100	168	68	94	0.1	87.2	11.9	0.9
100	504	72	100	Traces	87.1	12.1	0.8
70	2232	72	100	Traces	..	..	..

From small-scale experiments it was known that, at the beginning of polymerization, the products are mostly soluble ones; our experiments illustrate the effect of minute quantities of bridges formed during prolonged heating, which is necessary to produce good yields. The oxidizability decreases with reaction time, as may be seen from elementary analysis. The insoluble polymers have the mechanical properties of a slightly vulcanized rubber, but may easily be broken down by milling at low temperatures, which makes them partially soluble.

Small quantities of the catalyst are built into the polymer, as was found by nitrogen determination.

Polybutadiene.—The following two experiments made at 100° C with 1.25 per cent diazoaminobenzene as catalyst may serve as examples:

Time (hours)	Butadiene (grams)	Yield (grams)	Yield (percentage)	Percentage C (calc. 88.9)	Percentage H (calc. 11.1)	Residue 100% − (C + H)
116	67	33.6	50.3	88.1	10.8	1.1
340	70.5	42.2	60.4	89.3	10.7	0.0

After extraction with methanol, 0.04 per cent nitrogen was found in the first experiment. The low-boiling fractions consisted of about 10 per cent gases (starting material) and about 30 per cent of a dimeric fraction. From fractionation and refractive index determinations it became evident that aromatics from decomposition of the catalyst were also present as impurities. Correct figures for dimeric butadiene are: $b.p._{760}$, 129.4° C; n_D^{20}, 1.4637 (according to Harkness, Kistiakowski, and Mears[28]).

The fractionation, moreover, proves that no trimers or tetramers are present.

FRACTIONATION AND ANALYSIS OF DIMERIC PRODUCTS

Boiling point (° C)	n_D^{20}	Percentage C (calc. 88.9)	Percentage H (calc. 11.1)	C + H
121–126	1.4728	88.7	11.0	99.7
126–129	1.4636	88.9	11.1	100.0
129–133	1.4653	88.9	11.0	99.9
135–137	1.4694	..	..	..
170	1.4983	..	..	..

SUMMARY

The polymerization of dienes under the influence of heat, of diazoaminobenzene, and of benzoyl peroxide has been studied. Diazoaminobenzene probably acts as a slow but continuous source of free radicals, giving quantitative yields of methyl rubber of good quality from dimethylbutadiene after a few days to a few weeks at 100–125° C. The effect of diazoaminobenzene on butadiene is the same, but the rate of the uncatalyzed dimerization of butadiene at 100° C is as fast as that of dimethylbutadiene at 150° C and, therefore, dimerization interferes much more strongly with the polymerization of butadiene. Only 60 per cent of polybutadiene has been obtained. A few experiments with isoprene showed its position between the two other dienes. The effect of benzoyl peroxide on the polymerization of the dienes appeared to be much smaller than was expected from its known catalytic action on the polymerization of vinyl compounds, *e.g.*, styrene, for in this case its activity is about 100–1000 times greater than that of diazoaminobenzene. It is assumed that a larger number of radicals, produced by the fast decomposition of benzoyl peroxide, causes this difference. Diazoaminobenzene has about the same effect on the polymerization of styrene and acrylonitrile as on that of dienes. The catalytic effect of benzoyl peroxide on the polymerization of dienes is, on the contrary, 10,000–100,000 times smaller than on that of vinyl compounds. This difference can be understood by the assumption that the catalyst is quickly used up by oxidizing the dienes and their polymers. Whereas methyl rubber and the polyisoprene resemble raw natural rubber, polybutadiene, prepared under comparable conditions, is hard, swells moderately, and has a tendency to become brittle as a result of oxidation (aging).

ACKNOWLEDGMENT

The authors wish to thank J.W.F. van't Wout for his assistance in carrying out the laboratory experiments.

REFERENCES

[1] Whitby and Gallay, *Can. J. Research* **6**, 280 (1932).
[2] Kogerman, *Sitzer. Naturforsch.—Ges. Univ. Tartu* **41**, 3 (1934).
[3] Buizov, German Patent 521,903 (1932); *J. Applied Chem. U.S.S.R.* **6**, 1074 (1933).
[4] Schulz and Wittig, *Naturwissenschaften* **27**, 387 (1939); Schulz, *Naturwissenschaften* **27**, 659 (1939); *Z Elektrochem.* **47**, 265 (1941).
[5] Harries, *Ann.* **383**, 157 (1911).
[6] Levi, *Gomma* **1**, 4 (1937); RUBBER CHEM. TECH. **10**, 47 (1937).
[7] Khokhlovkin, *Sintet. Kauchuk* **5**, No. 4, 12 (1936); Lebedev, Khokhlovkin, Kuibina and Begetova, *Sintet. Kauchuk* **5**, No. 1, 2 (1936).
[8] Balandina, Berezan, Dobromyslova, Dogadkin and Lapuk, *Bull. acad. sci. U.R.S.S.* Ser. VII, **1946**, p. 423.
[9] Cuthbertson, Gee and Rideal, *Nature* **140**, 889 (1937).
[10] Schulz and Husemann, *Z. Physik. Chem.* **B36**, 194 (1937).
[11] Staudinger and Heuer, *Ber.* **67**, 1164 (1934).
[12] I. G. Farbenindustrie A.-G., German patent 631,527 (1936).
[13] Kern and Fernow, *J. prakt. Chem.* **160**, 281, 296 (1942).
[14] Gilman, "Organic Syntheses", Collective Vol. I, John Wiley & Sons, New York, p. 448.
[15] Kyriakides, *J. Am. Chem. Soc.* **36**, 987 (1914).
[16] Egloff, "Physical Constants of Hydrocarbons", Reinhold Publishing Corp., New York, **1939**, p. 311.
[17] Young, Vogt and Nieuwland, *Ind. Eng. Chem. Anal. Ed.* **8**, 198 (1936).
[18] Meyer, "Analyse und Konstitutionsermittlung Organischer Verbindungen," 6th Ed., Vol. 1, Springer Vienna, **1938**.
[19] Hershberg and Ruhoff, "Organic Syntheses", **17**, 25 (1937).
[20] Egloff, "Physical Constants of Hydrocarbons", Reinhold Publishing Corp., New York, **1939**, p. 303.
[21] Analysis performed by De Bataafsche Petroleum Mij.
[22] Harries and Gottlob, *Ann.* **383**, 228 (1911).
[23] Egloff, "Physical Constants of Hydrocarbons", Reinhold Publishing Corp., **1939**, p. 306.
[24] Waterman and de Kok, *Rec. trav. chim.* **53**, 1133 (1934).
[25] Van der Burg, *Rec. trav. chim.* **41**, 21 (1922).
[26] I. G. Farbenindustrie A.-G., German patent 496,372 (1930); example No. 4.
[27] Davis and Wiedeman, *Ind. Eng. Chem.* **37**, 482 (1945).
[28] Harkness, Kistiakowski and Mears, *J. Chem. Physics* **5**, 682 (1937).

ELASTIC DEFORMATION AND MOLECULAR WEIGHT IN POLYISOBUTYLENE *

JOHN REHNER, JR.

ESSO LABORATORIES, STANDARD OIL DEVELOPMENT COMPANY, ELIZABETH, N. J.

Although various properties of high polymers are known to depend on molecular weight, there appear to be no published data which show explicitly how the molecular weight of a rubberlike substance influences the modulus of high elasticity, even though a psychological perception of some such relationship has long existed. Also, the various expressions[1] that have been derived by statistical methods contain molecular weight as a factor ranging from an inverse first power up to inverse higher fractional powers.

Some time ago a need arose in this laboratory for estimating the average molecular weights of samples of polyisobutylene by a rapid procedure. Because of the slowness of polymer dissolution, methods based on measurements of the polymer in the dissolved state had to be ruled out and an investigation was, therefore, made of the rate of compression of a variety of samples in a Williams parallel-plate plastometer. It was found possible to render negligible the viscous component of deformation by using a sufficiently high compressive load and by limiting readings to an interval of about one minute. When the observed deformation values were plotted against the logarithm of time, straight lines were obtained. The slopes of the lines could be correlated, at least approximately, linearly with the reciprocal average molecular weights of the samples.

EXPERIMENTAL

The polymer was given one or two passes through a rubber mill (0.015-inch roll setting) and samples of the rolled material were molded for 15 minutes at 141° C to produce cylindrical specimens 0.5 inch high and 0.75 inch in diameter. The specimen was allowed to cool to room temperature, and was then placed between the plates of a Williams plastometer equipped with a total load of 15 kilograms. The weight was released and dial readings were taken at 10 second intervals for a period of 100 seconds. Some measurements were also carried out in a constant temperature room maintained at 25 ± 1° C. The deformation values could be duplicated to within 0.001 inch, using separate specimens of the same polymer. This corresponds to about a 5 per cent error in the deformation *vs.* reciprocal molecular weight plot for a polyisobutylene sample having a viscosity average molecular weight of about 1,500,000.

Molecular weights were determined viscometrically from intrinsic viscosities in diisobutylene[2]. The effect of the milling and molding operations on the molecular weight of the samples was also determined. The viscometric molecular weights were reproducible within about 5 per cent.

* Reprinted from the *Journal of Polymer Science*, Vol. 1, No. 3, pages 225–228, May 1946.

RESULTS AND DISCUSSION

A few typical plots of deformation *vs.* the logarithm of time are shown in Figure 1. After about one minute a significant departure from linearity is observed. It was found convenient to use the difference between the 10-second and the 60-second plastometer readings as a measure of the slope. Table I contains pertinent data for a series of polymers. The molecular weight results for Samples 14 to 18 show that the preparative procedure leads to an appreciable amount of polymer degradation, the average molecular weight (viscometric), $\bar{M}_v$, decreasing by 5 to 30 per cent. This is probably the result chiefly of the

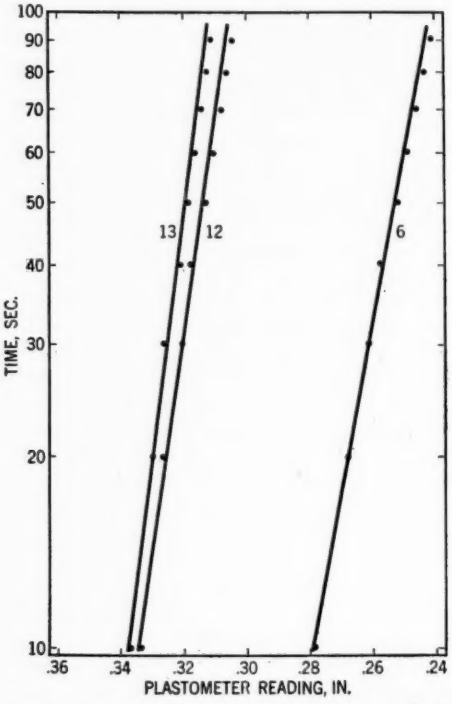


FIG. 1.—Typical deformation *vs.* log time curves for polyisobutylene. $\bar{M}_v$ (Sample 6) = 950,000; $\bar{M}_v$ (Sample 12) = 1,500,000; $\bar{M}_v$ (Sample 13) = 2,400,000.

molding treatment and might be reduced. The dependence of the rate of deformation on molecular weight is shown in Figure 2; here, $10^6/\bar{M}_v$ for the molded specimens has been plotted against the difference between the 10-second and 60-second deformation values. The dependence is linear within the probable experimental error, and it is seen that little if any advantage is gained from more careful temperature control.

According to the rationalized treatment by Alexandrov and Lazurkin[3], the high elastic component of deformation, D, of a polymer subjected to a stress, f, for a time t is given by:

$$D = (f/E)[1 - \exp(-t/\tau)] \quad (1)$$

where E is the modulus of high elasticity and τ is an orientation time. Differ-

TABLE I

MOLECULAR WEIGHT AND PLASTOMETER DATA FOR POLYISOBUTYLENES

Sample	$\bar{M}_v \times 10^{-3}$		Plastometer reading (inches)	
	Crude	Molded	10 seconds	60 seconds
1	..	460	0.261	0.217
2	..	470	0.245	0.208
3	..	580	0.276	0.2345
4	..	775	0.276	0.242
5	..	900	0.278	0.2465
6	..	950	0.279	0.2495
7	..	990	0.275	0.2425
8	..	1030	0.290	0.2595
9	..	1100	0.3025	0.2745
10	..	1160	0.2675	0.2415
11	..	1200	0.2935	0.2655
12	..	1500	0.334	0.3115
13	..	2400	0.337	0.3175
14[a]	840	630	0.289	0.2535
15[a]	1020	720	0.280	0.246
16[a]	1350	1090	0.292	0.2645
17[a]	1800	1700	0.319	0.293
18[a]	4400	4000	0.346	0.3355

[a] Deformed at 25 ± 1° C; all other samples deformed at room temperature.

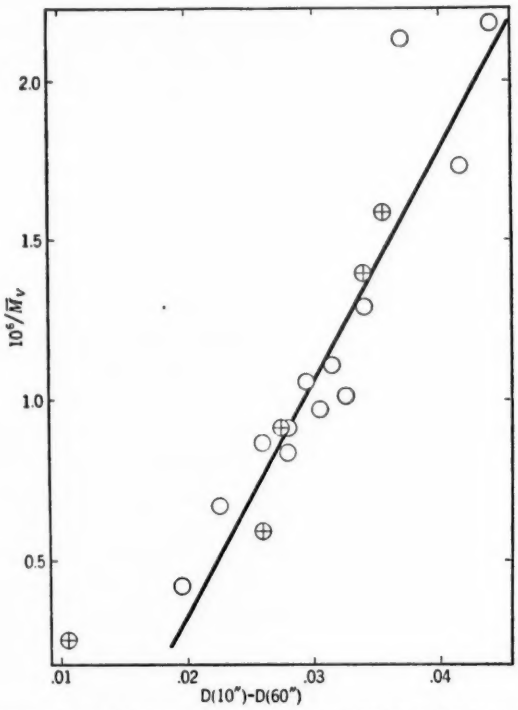


FIG. 2.—Dependence of rote of deformation on molecular weight for polyisobutylene. The open and the crossed circles refer, respectively, to experiments at room temperature and at 25 ± 1° C.

entiating Equation (1) with respect to ln t, and substituting into the result the values of t and of exp $(-t/\tau)$ obtained from (1), an equation is obtained which yields on integration:

$$|D| \cong (2f/E) \ln t + \text{constant} \tag{2}$$

provided that the values of f and D satisfy the condition $(ED/f) \ll 1$. The absolute value of D in Equation (2) is indicated because D, in compression, is negative. The above treatment assumes that the applied stress is constant; this is not true because of the changing dimensions of the samples during compression, but the assumption does not introduce a serious error and, furthermore, the error is partly compensated when the results for different samples are compared, as in Figure 2.

According to the experimental results shown in Figure 2:

$$\frac{d|D|}{d \ln t} \propto \frac{1}{\bar{M}_v} \tag{3}$$

Comparing Equations (2) and (3), E is seen to be functionally dependent on $\bar{M}_v$, at least approximately, as:

$$E \propto \bar{M}_v \tag{4}$$

rather than inversely as suggested by the formula of Kuhn[1] for linear polymers without cross-linkages. It would be of interest to learn whether Equation (4) applies to other polymers which are uncomplicated by branching or cross-linking. A thorough test of these relationships would of course require some attention to be paid to the effect of changing the applied stress and temperature. An application of deformation-rate measurements to fractionated samples of Butyl rubber, and to blends of the fractions, will be published in the near future[4].

ACKNOWLEDGMENT

The author wishes to express his appreciation to A. M. Gessler and S. B. Robison for preparing the samples and carrying out most of the deformation measurements.

REFERENCES

[1] Meyer and Van der Wyk (*J. Polymer Science* **1**, 49 (1946)) have tabulated some of these derived expressions
[2] Flory, *J. Am. Chem. Soc.* **65**, 372 (1943).
[3] Aleksandrov and Lazurkin, *Acta Physicochim. U.R.S.S.* **12**, 647 (1940).
[4] R. L. Zapp and F. P. Baldwin, private communication.

APPLICATIONS OF ULTRAVIOLET SPECTROGRAPHY. A STUDY OF SOME ACCELERATORS *

CHARLES DUFRAISSE AND JEAN HOUPILLART

INSTITUT FRANÇAIS DU CAOUTCHOUC, PARIS, FRANCE

Not only is the problem of determining the compounding ingredients originally present in a rubber mixture by an analysis of the vulcanized product of interest from a technical point of view, but it also is of importance from the theoretical point of view to know what becomes of these ingredients as a result of the thermal effects of vulcanization. This is particularly true of that class of ingredients which function as accelerators of vulcanization.

Chemical methods which are applicable to this problem are in all cases very complicated and are inconvenient in various ways. For some ingredients there are no methods at all available. Accordingly it was thought that a study of ultraviolet spectra, the general principles of which have already been described[1] and which have already been utilized by Jarrijon for the determination of antioxygenic substances[2], might offer a more rapid and more reliable means of attaining the desired end.

The aim of the experiments to be described was simply to show what is to be expected of the method in this particular practical application. The study was devoted to three accelerators: diphenylguanidine, benzothiazyl disulfide, and mercaptobenzothiazole.

Mixtures of the following base composition containing the three accelerators:

Pale crepe	100
Sulfur	3
Accelerator	1
Zinc oxide	2

were prepared by milling 300 grams of pale crepe on a cold roll mill until it was well plasticized (35 minutes), then adding 9 grams of sulfur during 10 minutes and 6 grams of zinc oxide during 5 minutes. The mixture was then divided into three equal parts, to each of which was added, during 5 minutes, 1 gram of the particular accelerator.

The conditions of vulcanization naturally varied with the nature of the accelerator, but in each case the final mixture was divided into two equal parts, which were subjected to two different thermal treatments:

(1) normal vulcanization, so that the optimum mechanical properties were obtained.
(2) decided undervulcanization.

The time of heating to obtain considerably undervulcanized samples was chosen so as to bring each mixture to a state approaching the point of setting, *i.e.*, to the point at which it is set enough to be capable of being removed from the mold but insufficiently to be regarded as vulcanized, and when cut surfaces can be stuck together again.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 19, No. 7, pages 207–211, August 1942.

DIPHENYLGUANIDINE MIXTURE

Undervulcanized mixture.

By thermal treatment for 15 minutes at 125° C, the product was plastic and, like crepe rubber which has undergone prolonged milling, had no mechanical strength. Extraction of 20 grams of the undervulcanized mixture yielded 0.985 gram of dry substances. The extraction flask contained 0.302 gram of crystalline sulfur; the extraction liquor, of a deep brown color, was saturated with sulfur. This sulfur was separated by evaporating the acetone, treating the residue with 10 cc. of absolute alcohol, and filtering. This gave 0.101 gram of sulfur. The rubber mixture therefore contained 0.403 gram of free sulfur. Consequently only about 7 per cent of the sulfur contained in the original rubber mixture was found in the combined state.

The resins remaining after evaporation of the alcoholic solution weighed 0.680 gram. They were dissolved in chloroform for spectrographic examination.

Absorption was weak, and became manifest only with solutions containing 0.4 gram per liter. There was no absorption band, as with diphenylguanidine, and the spectral figure resembled more nearly that which is obtained with extracts of crude rubber.

Normally vulcanized mixture.

When heated in a press for 75 minutes at 145° C, the same mixture as that described above gave a vulcanizate with good mechanical properties and which contained no free sulfur separable by the technique employed. Extraction with acetone gave a dark yellow solution, the dry residue from which, weighing 0.745 gram, *i.e.*, 3.7 per cent of the product which was extracted, was almost wholly soluble in 98% alcohol, and did not yield any sulfur. In chloroform solutions of various concentrations, its spectrum showed that it had very little absorptive power. The values which were obtained were identical with those corresponding to the extract of the undervulcanized mixture, but the absorption was in general not quite so weak.

The results of these tests show that, from the beginning of vulcanization, diphenylguanidine can no longer be extracted by acetone. This leads to the question as to what becomes of it during heating in the presence of the various components of the rubber mixture.

Discussion of the results.

The pyrogenic decomposition of diphenylguanidine was studied by Rathke[3]. He came to the conclusion that, by heating at 170° C, two reactions may take place simultaneously, with formation of ammonia, aniline, and the compounds, $C(NC_6H_5)_2$ and $NCNHC_6H_5$. The final product of the reaction would be a complex of these last two compounds.

If the reactions proceed in the same way in the rubber mixtures which were studied, the extracts should give a characteristic spectrum.

On the other hand Bruni and Levi[4] studied the action of sulfur on diphenylguanidine, and obtained, at 260–270° C, mercaptobenzothiazole, though probably in low yields. It might well be asked whether the disappearance of diphenylguanidine is not explained by the reaction of Bruni and Levi. If so, the mercaptobenzothiazole which is formed should be recovered in the extracts in the form of a mixture with benzothiazyl disulfide, which is very easy to characterize.

Consequently it may be concluded that the reaction described by Bruni and Levi did not, under the conditions employed in the present work, take place except to a negligible extent.

Finally Wistinghausen[5] used chemical methods to study diphenylguanidine in vulcanized mixtures. The acetone extract was extracted with hydrochloric acid and the diphenylguanidine precipitated by picric acid. In this way Wistinghausen was successful in finding considerable quantities of diphenylguanidine in his rubber mixtures, and he found that it disappeared completely only in mixtures with relatively high percentages of sulfur (5 per cent) and zinc oxide (12 per cent).

In the present work, qualitative tests for diphenylguanidine in the extracts were made by means of picric acid. The extract of the normally vulcanized mixture gave no yellow precipitate. On the contrary, the extract of the undervulcanized mixture gave a positive reaction, although the amount of precipitate obtained was so small that the diphenylguanidine which it represented could not be detected spectrographically. A control experiment showed that the reaction with picric acid is very sensitive; however, it is not necessarily specific to diphenylguanidine, because compounds of numerous organic substances with this acid are known. In short, the results of Wistinghausen seem not to be in accord with those of the present work; however, this disagreement is only apparent.

Actually the hypothesis which seems to be the most plausible in explaining the complete absence of diphenylguanidine in the acetone extract is to assume the formation of a compound which resists extraction by acetone by virtue of its insolubility. This hypothesis is in good accord with experiments of Humphrey[6], who showed that it is necessary only to add a little hydrochloric acid to the acetone to obtain diphenylguanidine in the acetone extract.

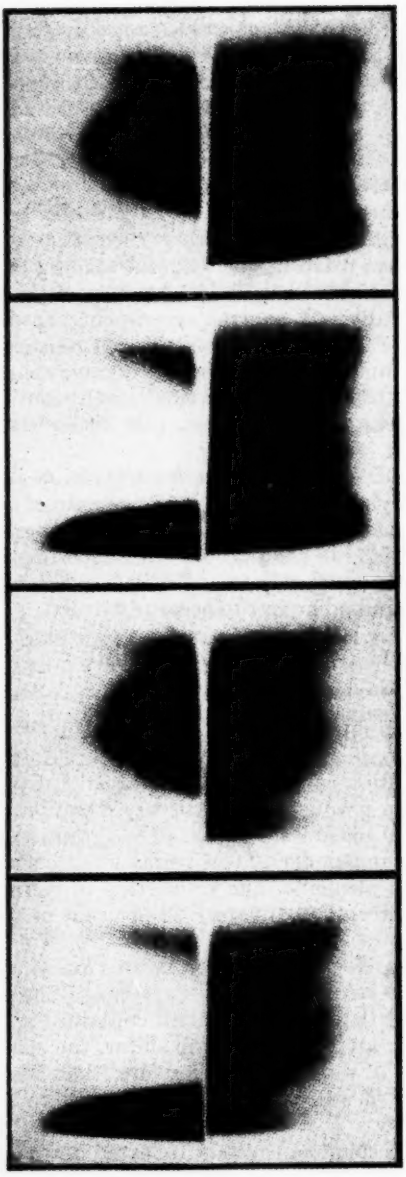
BENZOTHIAZYL DISULFIDE MIXTURE

Undervulcanized mixture.

Thermal treatment for 10 minutes at 145° C gave a product which had all the characteristics of being considerably undervulcanized. Extraction with acetone gave a pale yellow solution containing 1.300 grams of dry substances, representing 6.5 per cent of the product submitted to extraction. The total amount of sulfur recovered was 0.450 gram. A part (0.363 gram) was recovered from the acetone solution; the remainder (0.086 gram) was isolated by treatment of the dried extract with alcohol. The proportion of sulfur combined with the rubber was consequently approximately 20 per cent of the quantity added.

The remainder of the extract, weighing 0.861 gram, was examined in chloroform solution by ultraviolet spectrography. The spectra of the solutions of different concentrations showed that the extract still contained a little sulfur, but that, aside from absorption attributable to the sulfur, the spectral figures were practically nonexistent. It would seem, therefore, that the accelerator disappears from the beginning of vulcanization by passing into an insoluble state.

At the end of several weeks, colorless crystals appeared on the walls of the receptacles containing the chloroform solutions of the extract. These were almost wholly insoluble in chloroform, ether, acetone and benzene, even when hot. They melted to a paste at 165–167° C. A saturated solution in chloroform did not absorb ultraviolet radiation appreciably, probably because the



a b c d

FIG. 1.—Benzothiazyl disulfide mixture. Comparison of the spectra of two fractions of the extract with the spectra of mercaptobenzothiazole and benzothiazyl disulfide.

a. (Upper) mercaptobenzothiazole (0.1 g. per l.).
(Lower) dissolved part of extract (1 g. per l.).
b. (Upper) benzothiazyl disulfide (0.1 g. per l.).
(Lower) dissolved part of extract (1 g. per l.).
c. (Upper) mercaptobenzothiazole (0.1 g. per l.).
(Lower) undissolved part of extract (1 g. per l.).
d. (Upper) benzothiazyl disulfide (0.1 g. per l.).
(Lower) undissolved part of extract (1 g. per l.).

concentration was not high enough. These facts alone show that the product is neither sulfur nor benzothiazyl disulfide, but so little was formed that it was impossible to make any further tests in an effort to identify the product.

Normally vulcanized mixture.

The normally vulcanized mixture was prepared by heating in a press for 40 minutes at 145° C. Extraction of 20 grams with acetone gave 0.695 gram of acetone extract, which, treated with 10 cc. of absolute alcohol, gave a fraction weighing 0.415 gram soluble in alcohol. The alcohol-soluble portion and the residue were dissolved in chloroform and examined spectrographically. The two solutions gave spectrographs of essentially the same structure, and differed only in the intensities of the bands, *i.e.*, the alcohol-insoluble portion gave a stronger band than did the soluble portion (see the lower spectra in Figure 1).

The spectra showing the absorption of these extracts were compared with those of mercaptobenzothiazole and of benzothiazyl disulfide in chloroform solutions, at concentrations first of 1 gram per liter and then 0.1 gram per liter.

A cursory examination of these spectrographs leads to the conclusion that the extract is composed of a mixture of mercaptobenzothiazole and benzothiazyl disulfide. This is supported by the data in Table 1, which showed, for each of the spectra, the wave lengths of the absorption maxima which were observed.

TABLE 1

Mercapto-benzothiazole	Benzothiazyl disulfide	Portion of extract soluble in alcohol	Portion of extract insoluble in alcohol
3280	—	3250	3240
—	3030	3025	—
—	2920	2900	2750
2610	2770	2760	2590
2560	—	—	2610
—	—	—	—

The benzothiazyl disulfide contents of the two fractions of the extract appear to be almost the same; on the contrary, the mercaptobenzothiazole is concentrated chiefly in the insoluble portion.

In summary, the phenomena which were observed in the case of mixtures accelerated by benzothiazyl disulfide, may be explained as follows. When a mixture is heated under conditions such that it is very much undervulcanized, no trace of the accelerator originally added, or of any products into which it might have been transformed, is found in the acetone extract. The spectrum resembles that of the rubber resins. On the contrary, when the mixture is vulcanized to the correct point, the acetone extract gives a characteristic spectrum which indicates the presence of mercaptobenzothiazole and benzothiazyl disulfide.

These results lead to the conclusion that, in accelerated mixtures, the reactions which one or the other of these products undergo are not wholly independent of each other. For this reason it seemed more interesting to analyze the results obtained with benzothiazyl disulfide at the same time as those obtained in the study of mercaptobenzothiazole mixtures.

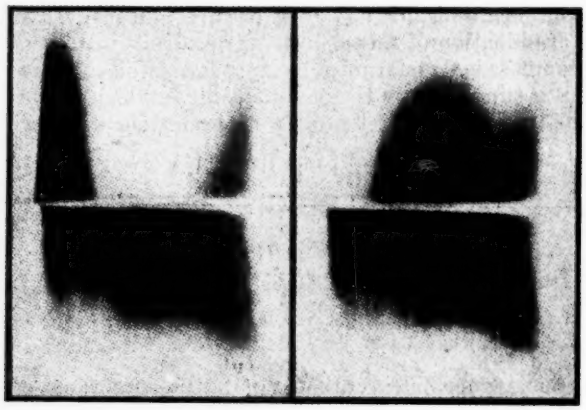
MERCAPTOBENZOTHIAZOLE MIXTURE

Undervulcanized mixture.

When the mercaptobenzothiazole mixture was heated for 5 minutes at 145° C, the product was very soft and tacky. Extraction of 20 grams by ace-

tone gave 1.251 grams of dry substances, representing 6.2 per cent of the original rubber mixture. Among the substances extracted, the first was sulfur, the weight of which was 0.456 gram, and which was separated from the extracted acetone solution. The dry extract was treated, as in other experiments, with 10 cc. of absolute alcohol, but the results obtained were unexpected, for the extract contained products other than sulfur which were insoluble in alcohol and which hindered separation of the sulfur. However, no attempt was made to carry the fractionation further, for the product which it was desired to isolate, *viz.*, mercaptobenzothiazole, was assumed, because of its high solubility, to be concentrated wholly in the alcoholic liquor.

The portion of the extract which was soluble in alcohol weighed 0.447 gram. In chloroform solution, its spectrum appeared as shown in Figures 2a and 2b, where it is compared with the spectra of mercaptobenzothiazole and benzothiazyl disulfide.



a *b*

FIG. 2.—Undervulcanized mercaptobenzothiazole mixture.
a. (Upper) mercaptobenzothiazole (0.1 g. per l.).
(Lower) dissolved part of extract (1 g. per l.).
b. (Upper) benzothiazyl disulfide (0.1 g. per l.).
(Lower) dissolved part of extract (1 g. per l.).

The wave lengths of the absorption maxima are summarized in Table 2.

Table 2 and Figure 2 indicate that the extract was composed of a mixture of mercaptobenzothiazole and benzothiazyl disulfide. Furthermore the spectra, although representing a concentration of extract of 1 gram per liter, are not intense; this is an indication of a small proportion of the two products having these characteristic spectra.

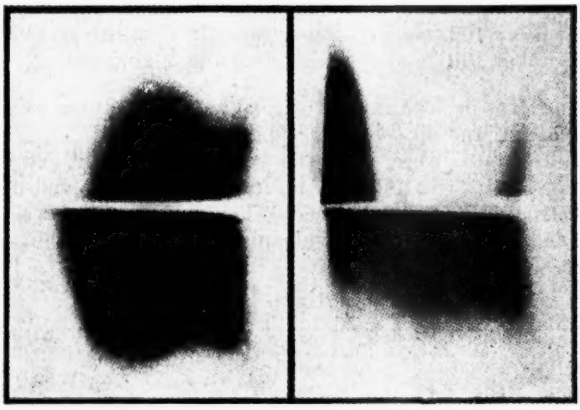
TABLE 2

Mercaptobenzothiazole	Benzothiazyl disulfide	Extract (1 gram per liter)
3280	—	3250
—	3030	3040
—	2920	2930
—	2770	—
2610	—	2600
2560	—	2550

Normally vulcanized mixture.

In this case the mixture was heated for 40 minutes at 145° C. Extraction of 20 grams with acetone gave 0.584 gram of dry substances. Treatment of the extract with 10 cc. of absolute alcohol extracted 0.503 gram of alcohol-soluble substances. This fraction and the undissolved residue were dissolved in chloroform and examined spectrographically. Figure 3 shows their spectra compared with the spectra of benzothiazyl disulfide and mercaptobenzothiazole.

The tops of the bands correspond to the wave lengths shown in Table 3.



a *b*

FIG. 3.—Normally vulcanized mercaptobenzothiazole mixture.
a. (Upper) benzothiazyl disulfide (0.1 g. per l.).
(Lower) dissolved part of extract (1 g. per l.).
b. (Upper) mercaptobenzothiazole (0.1 g. per l.).
(Lower) undissolved part of extract (0.3 g. per l.).

TABLE 3

Mercapto-benzothiazole (0.1 g. per liter)	Benzothiazyl disulfide (0.1 g. per liter)	Portion of extract dissolved in alcohol (0.1 g. per liter)	Portion of extract not dissolved in alcohol (0.3 g. per liter)
3280	—	—	3270
—	3030	3020	3030
—	2920	2940	2910
—	2770	2800	2750
2610	—	—	—
2560	—	—	—

An examination of the data in Table 3 and of Figure 3 leads to the conclusion that the extract contained mercaptobenzothiazole and benzothiazyl disulfide, which were present in much higher percentages than they were in the extract of the same mixture which had been undervulcanized. The higher proportions in the extract of the normally vulcanized mixture are evident by a comparison of the spectra in the lower halves of Figure 3a and Figure 2a, which represent practically equal intensities, in spite of the concentrations being very different, *viz.*, 0.3 gram per liter in the first case and 0.1 gram per liter in the second case.

On the other hand the bands of mercaptobenzothiazole itself are not intense, either for the portion of the extract soluble in alcohol or for the undissolved portion. The extract contained, therefore, only a small percentage of mercaptobenzothiazole.

Incomplete mixtures.

It was of interest to determine whether mercaptobenzothiazole is transformed in a similar way when mixtures which do not contain all the vulcanizing ingredients, *viz.*, sulfur, accelerator and zinc oxide, are heated under the conditions used in preparing the undervulcanized and normally vulcanized mixtures. In other words, does the absence of sulfur or zinc oxide, or both, modify the nature of the reactions which the accelerator undergoes?

The following three mixtures were prepared:

(A) crepe rubber 100, mercaptobenzothiazole 1;
(B) crepe rubber 100, mercaptobenzothiazole 1, sulfur 3;
(C) crepe rubber 100, mercaptobenzothiazole 1, zinc oxide 2.

Each mixture was divided into two equal parts, and these were heated in a press at 145° C for 5 and 40 minutes, respectively.

The six vulcanizates were extracted with acetone; the extracts, freed of sulfur when present by treatment with alcohol, were dissolved in chloroform, and their spectrographs were obtained. Table 4 gives the weights of these extracts obtained from 20 grams of vulcanizate.

TABLE 4

Mixture	Time of heating at 145° C (min.)	Weight of total extract (grams)	Weight of free sulfur (grams)	Weight of extract without sulfur (grams)
A_1	5	0.762	—	0.762
A_2	40	0.731	—	0.731
B_1	5	1.179	0.504	0.675
B_2	40	0.791	0.059	0.732
C_1	5	0.661	—	0.661
C_2	40	0.676	—	0.676

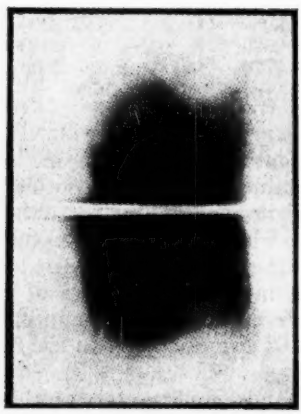


FIG. 4.—Crepe-mercaptobenzothiazole mixture.
(Upper) benzothiazyl disulfide (0.1 g. per l.).
(Lower) extract (0.4 g. per l.).

All the spectra obtained were identical in character, and represented the adsorption of benzothiazyl disulfide accompanied by a slight general absorption due to the presence of resins (see Figure 4). In addition, examination of rather concentrated solutions indicated that the extracts contained a little mercaptobenzothiazole.

These spectra showed only small differences in intensity; however, the extract of mixture A_1 had the highest content of benzothiazyl disulfide, and the extracts of mixtures C_1 and C_2 the lowest contents of benzothiazyl disulfide.

Figure 4 shows a comparison of the spectrum of extract A_1 with that of the extract of benzothiazyl disulfide. The absorptions resemble each other fairly closely, from which it may be concluded, taking into account the different concentrations of the solutions, that the benzothiazyl disulfide content of extract A_1 was of the order of 25 per cent. In weight this meant that 0.762×0.25 or 0.190 gram was extracted from the 20 grams of vulcanizate. Since 20 grams of the original mixture contained 0.2 gram of mercaptobenzothiazole, the yield of benzothiazyl disulfide by transformation of mercaptobenzothiazole was approximately 80 per cent.

DISCUSSION OF THE RESULTS

In discussing in their entirety the results obtained with the benzothiazyl disulfide mixture and mercaptobenzothiazole mixture, it is well first to summarize the phenomena which were observed.

(1) *The benzothiazyl disulfide mixture.*

(a) When the mixture was undervulcanized, practically no trace of any accelerator was found in the extract.

(b) When the mixture was vulcanized correctly, the extract contained mercaptobenzothiazole and benzothiazyl disulfide.

(2) *The mercaptobenzothiazole mixture.*

(a) When the mixture was undervulcanized, spectrographic analysis indicated the presence of small amounts of mercaptobenzothiazole and benzothiazyl disulfide.

(b) When the mixture was correctly vulcanized, greater amounts of mercaptobenzothiazole and benzothiazyl disulfide were found, with the latter predominating.

(c) With incomplete mixtures (absence of sulfur, zinc oxide, or both), there was in all cases extensive transformation of mercaptobenzothiazole into benzothiazyl disulfide.

Under the conditions, therefore, there was a temporary disappearance of the accelerator[7], probably by formation of a compound which was not extractable by acetone. This compound probably then decomposed, with liberation of the accelerator by the time vulcanization was complete.

However, this accelerator was not found in its original form alone; part was transformed into another compound; benzothiazyl disulfide was transformed in part into mercaptobenzothiazole, mercaptobenzothiazole in part into benzothiazyl disulfide. Furthermore in incomplete mixtures, even those which cannot be vulcanized, mercaptobenzothiazole changes into benzothiazyl disulfide. This last fact is in disagreement with the theory of Seide and Petrov[8], according to which the opposite transformation should take place.

These preliminary and simple experiments will have to be continued before it is possible to draw any more definite conclusions. In particular, it will be

necessary to determine whether, as seems probable, an equilibrium is established between benzothiazyl disulfide and mercaptobenzothiazole, what are the proportions of the two components, and what factors displace this equilibrium.

However it may be, these tests have already shown that when mercaptobenzothiazole or benzothiazyl disulfide is employed as an accelerator, the compositions of the acetone extracts of the respective vulcanizates are similar and each contains a mixture of these two accelerators. This is in accord with hypotheses proposed to explain the mechanism of their action.

REFERENCES

[1] Dufraisse and Houpillart, *Rev. gén. caoutchouc* **16**, 44 (1939).
[2] Jarrijon, *Rev. gén. caoutchouc* **18**, 217 (1941); and the following article in this issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[3] Rathke, *Ber.* **20**, 1065 (1887).
[4] Bruni and Levi, *Atti acad. Lincei* [5] **32**, 313 (1923).
[5] Wistinghausen, *Kautschuk* **5**, 57, 75 (1929).
[6] Humphrey, *Ind. Eng. Chem. Anal. Ed.* **8**, 153 (1936).
[7] The fact that small amounts of the two accelerators were found in the undervulcanized mercaptobenzothiazole mixture, whereas practically no trace of accelerator was found in the undervulcanized benzothiazyl disulfide mixture, may be attributed to the different states of vulcanization.
[8] Seide and Petrov, *J. Rubber Ind.* **12**, 665 (1935).

APPLICATIONS OF ULTRAVIOLET SPECTROGRAPHY. A STUDY OF THE TRANSFORMATIONS WHICH TETRAMETHYLTHIURAM DISULFIDE UNDERGOES DURING THE VULCANIZATION PROCESS *

ANDRÉ JARRIJON

INSTITUT FRANÇAIS DU CAOUTCHOUC, PARIS, FRANCE

INTRODUCTION

Numerous investigators have attempted to explain the behavior of tetramethylthiuram disulfide as a direct vulcanizing agent by certain chemical transformations which they have concluded that it undergoes. However, in most cases these transformations have been based merely on hypotheses or, where the author has depended on known facts, these facts have borne no direct relation to the conclusions which have been drawn.

As a result of the work of Bruni[1] it has been a very widely accepted theory that tetramethylthiuram disulfide reacts by changing into the corresponding monosulfide with liberation of one atom of sulfur from each molecule of disulfide. It has also been often assumed that it undergoes pyrolysis, with formation of tetramethylthiourea.

Since it is necessary to add zinc oxide as an accessory agent to obtain a vulcanizable mixture, it has also been reasoned further that zinc salts capable of bringing about vulcanization are formed. Some investigators, particularly Cummings and Simmons[2], have thought that the zinc salt might be zinc dimethyldithiocarbamate; others, more numerous, have rejected this hypothesis, *e.g.*, Twiss, Brazier and Thomas[3], and Grenness[4], for, as they say, zinc dimethyldithiocarbamate is not capable of bringing about vulcanization in the absence of sulfur. Grenness assumed the existence of zinc polysulfides of rather complex consitutions, without, however, isolating them or even identifying them.

As Cummings and Simmons point out, only experiments having as their aim the isolation of the reaction products of accelerators during vulcanization would be expected to throw any light on the mode of action of these substances.

It is this problem which we have undertaken to solve in the case of tetramethylthiuram disulfide, when used as a vulcanizing agent in the absence of sulfur, by means of the delicate method of observation possible by the spectrographic method.

GENERAL SURVEY

In these experiments, the details of which will be discussed further on, the following simple mixture was used:

Rubber	100
Tetramethylthiuram disulfide	3
Zinc oxide	2

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 20, No. 8, pages 155–157, August 1943, and No. 9, pages 177–182, September 1943.

FIG. 1.

a. Spectrum of acetone extract of the vulcanized mixture (concentration 0.4 gram per l.).
b. Spectrum of tetramethylthiuram disulfide (concentration 0.2 gram per l.).
c. Spectrum of tetramethylthiuram monosulfide (concentration 0.3 gram per l.).
d. Spectrum of tetramethylthiourea (concentration 0.1 gram per l.).
e. Spectrum of zinc dimethyldithiocarbamate (concentration 0.2 gram per l.).

By extraction of the vulcanizate with acetone[5] it was possible to obtain from the extract the products which it was intended to study.

The absorption spectrum of this extract is a characteristic one, as shown in Figure 1a. The maximum absorption lies in the range of wave lengths of 2800 and 2600 Å.U., whereas tetramethylthiuram disulfide shows only a single band at 2650 Å.U. (Figure 1b). Consequently tetramethylthiuram disulfide is transformed during vulcanization, and so the problem was to identify the product of this transformation. This transformation product is not tetramethylthiuram monosulfide[6], for this compound has only one absorption band, which is very broad and lies at about 2750 Å.U. (see Figure 1c). Nor is the product tetramethylthiourea, which also has only one band, which is very narrow and lies at about 2500 Å.U. (see Figure 1d). As has already been pointed out[7], the transformation product is a product whose absorption spectrum is identical with that of zinc dimethyldithiocarbamate (see Figure 1e).

This confirms the observations of Shepard[8] and of Shimada[9], who came to the conclusion that zinc dimethyldithiocarbamate was present in their vulcanized rubber mixtures. The character of their experiments, which were based on color reactions, do not lend themselves to absolute precision, and for this reason they have not received much attention.

But what is more important, even if the identity of zinc dimethyldithiocarbamate is assumed to be an established fact, there is nothing in the earlier literature concerning the amount formed during vulcanization. The importance of the spectrographic method is particularly evident in this respect, for it makes possible an easy and rapid determination. By determining the concentration of the acetone extract, which gives a sharp spectral figure similar to that of pure zinc dimethyldithiocarbamate, a first approximation is obtained, provided that the relation between the weight of rubber extracted and the weight of the extract as well as the concentration of the solution being compared are known. The use of a comparator makes it possible to obtain better results. With this instrument it was proved that 70 to 76 per cent of the tetramethylthiuram disulfide is transformed into zinc dimethyldithiocarbamate. This makes invalid any theories based on too simple hypotheses which have been generally accepted up to the present time.

In view of the importance of this finding, it was necessary to check it with the utmost precision. By the combined use of two solvents, acetone and alcohol, it was possible to separate zinc dimethyldithiocarbamate from rubber and to isolate in the crystalline state 90 per cent of the quantity found by the spectrographic determination. When the product had been thoroughly purified, it appeared in the form of crystals (Figure 2a) similar to pure zinc dimethyldithiocarbamate (Figure 2b). The melting point and analytical determinations of sulfur, nitrogen and zinc confirmed the identity of the two compounds.

Further experiments proved that the transformation of tetramethylthiuram disulfide into zinc dimethyldithiocarbamate takes place during vulcanization and that there is no other contributing factor, such as the simple effect of heat, as might be indicated by the experiments of Maximoff[10] or the intervening action of an agent like the acetone used for extracting.

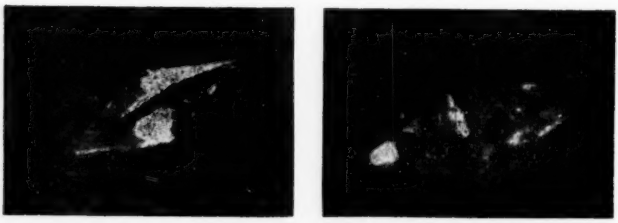
Grenness[4] has shown that it is possible, in benzene, to form zinc dimethyldithiocarbamate from tetramethylthiuram disulfide and zinc oxide under certain well defined conditions. The hydrogen necessary for the formation of water with the oxygen of the oxide is not attributable to the benzene for, by repeating and completing the experiments of Grenness, no evidence could be obtained of

the formation of biphenyl, which is the product most likely to be formed by the dehydrogenation of benzene.

Under the conditions prevailing in vulcanization the hydrogen should be furnished by the rubber, because it was proved that, without rubber, no zinc dimethyldithiocarbamate is formed under the same thermal conditions as those of vulcanization, and because, in addition, without the formation of zinc dimethyldithiocarbamate, no vulcanization of rubber takes place.

It is particularly significant in this respect that tetramethylthiuram monosulfide requires, in order to bring about vulcanization, a minimum addition of sulfur, such that the total monosulfide plus sulfur corresponds to the disulfide, since after vulcanization two-thirds of the monosulfide is found to be transformed into zinc dimethyldithiocarbamate just as if tetramethylthiuram disulfide had been added.

It has frequently been suggested that proteins and fat acids present in rubber play a part in the vulcanization process. But in the present problem, it is certain that they do not play any part in furnishing hydrogen, for in experiments with deproteinized rubber and with rubber from which the fat acids had been removed by extraction with acetone, the same results in every way were obtained.



a *b*

FIG. 2.

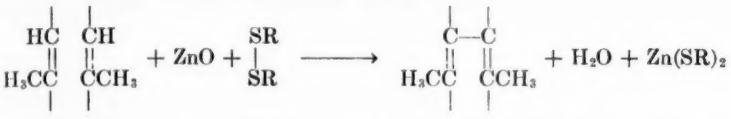
a. Zinc dimethyldithiocarbamate extracted from the vulcanized mixture and crystallized from acetone (magnification 23 times).
b. Pure zinc dimethyldithiocarbamate crystallized from boiling acetone (magnification 81 times).

As a matter of fact, the dehydrogenation of rubber hydrocarbon is classic and is well known. In the case of ebonite vulcanized by sulfur, even explosions sometimes occur as a result of the evolution of hydrogen sulfide.

The phenomenon observed with tetramethylthiuram disulfide cannot be exactly the same. It should, rather, involve a mild dehydrogenation which is preferentially confined to certain parts of the molecule and in addition without evolution of hydrogen sulfide. In reality if, with the vulcanizate indicated at the beginning, only a part of the tetramethylthiuram disulfide is transformed into zinc dimethyldithiocarbamate, there remains in the rubber 0.35 per cent of nonextractable sulfur, which represents exactly the sulfur of the tetramethylthiuram disulfide not found in the zinc dimethyldithiocarbamate. However, since this quantity is wholly insufficient to effect vulcanization, it must be concluded that, at best, the unidentified sulfur compound, the nature of which is unknown, brings about an accessory vulcanizing effect which adds itself to the vulcanizing effect resulting from the dehydrogenation reaction.

It is possible to explain in the following way how the dehydrogenation of rubber, which is manifest by the formation of zinc dimethyldithiocarbamate,

brings about the formation of a vulcanized structure:



Secondary phenomena which it is not easy to differentiate from the principal phenomenon are involved simultaneously with the latter.

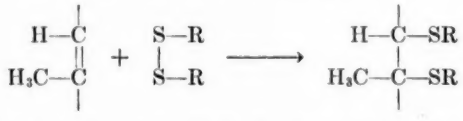
It is not possible to determine what becomes of the tetramethylthiuram disulfide which is not transformed into zinc dimethyldithiocarbamate. However, since tetramethylthiuram monosulfide, when heated in rubber under the same conditions as tetramethylthiuram disulfide, *i.e.*, in the absence of sulfur, does not yield any zinc dimethyldithiocarbamate, it can at least be said that the small quantity of sulfur thus rendered active—one-tenth of the proportion generally combined with rubber by vulcanization with sulfur—does not originate from the decomposition of tetramethylthiuram disulfide into tetramethylthiuram monosulfide. Added to the sulfur in the zinc dimethyldithiocarbamate, it indicates that the determinations are fairly exact, since the sulfur introduced by the tetramethylthiuram disulfide is entirely and exactly recovered.

This means, therefore, a verification of the operating technique and at the same time a confirmation of the conclusions which have been drawn.

Furthermore by analogy with certain other domains of organic chemistry, it is possible to conceive of a series of more complex reactions which account at the same time for the fixation of a certain amount of sulfur on the rubber, the formation of zinc dimethyldithiocarbamate, and the formation of a vulcanized structure.

It is known, in fact, that double bonds are capable of opening and then fixing certain molecules, with corresponding decrease in unsaturation. As an example, tetramethylthiuram disulfide can undergo scission into two equal parts, since it forms, for example, zinc dimethyldithiocarbamate:

There is no theoretical reason why this scission should not make possible a fixation on the double bonds of rubber according to the following scheme:



Two molecules of rubber on which the tetramethylthiuram disulfide becomes fixed in this way can then react with two normal molecules and a molecule of zinc oxide, in accordance with the scheme shown in the upper part of Figure 3.

According to this reaction, one of the two molecules of tetramethylthiuram disulfide which enter into the reaction becomes fixed on the rubber, while the other forms zinc dimethyldithiocarbamate; at the same time two double bonds become saturated and intermolecular bridges are formed. Two of the sulfurized groups formed in this way can in turn react with two rubber molecules and one zinc oxide molecule, as shown in the lower scheme of Figure 3. In

principle, there is no reason why this process should not continue, with formation of longer and longer chains.

However, it should be noted that the longer these chains are, the greater are the number of double bonds which are saturated by fixation of a molecule of tetramethylthiuram disulfide. Now, in a study of the same mixture, Hauser and Brown[11] observed that, for each atom of combined sulfur, there was a loss of approximately one double bond. An examination of the last scheme will show that it corresponds to the disappearance of exactly four double bonds per molecule of tetramethylthiuram disulfide which is fixed (*i.e.*, 4 atoms of sulfur). This is the proportion indicated by Hauser and Brown, and so one is led to conclude that, from a statistical point of view, the reaction stops at this stage.

It is evident, moreover, that, of the four molecules of disulfide which enter into the reaction, three molecules form zinc dimethyldithiocarbamate. This 75 per cent transformation is very close to the values of 70–76 per cent which

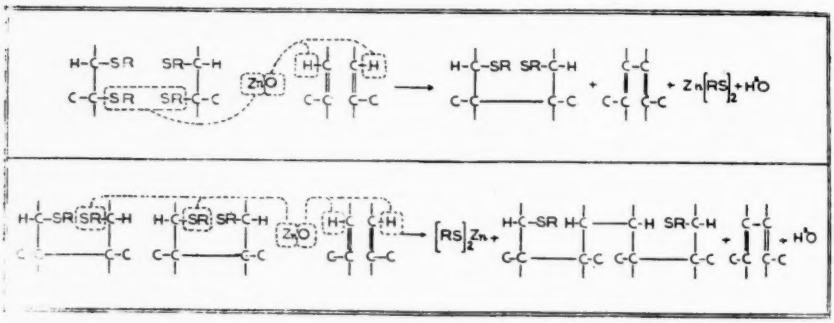


FIG. 3.—Schematic representation of reactions of tetramethylthiuram disulfide.

were obtained experimentally. Accordingly the scheme of reactions described above is in good agreement with various experimentally established facts, *e.g.*, the fixation of sulfur, the proportion of zinc dimethyldithiocarbamate formed, and the decrease in unsaturation. It therefore offers a plausible explanation of the mechanism of this particular mode of vulcanization.

DETAILED DESCRIPTION OF THE EXPERIMENTS

OPERATING CONDITIONS AND RESULTS

Mixture studied.

The composition of the mixture which was chosen for the experiments was the following:

Pale crepe	100
Tetramethylthiuram disulfide	3
Zinc oxide	2
Thickness of samples	2 mm.
Time of vulcanization	30 minutes at 125° C

The vulcanizate prepared in this way had a tensile strength of the order of 160 kg. per sq. cm., which indicates satisfactory vulcanization for a mixture of this type.

By extraction with acetone, the vulcanizate gave an extract which contained, in addition to the accelerator or its transformation products, only rubber resins.

Treatment of the mixtures. Preparation of the solutions.

Approximately one gram of the mixture (weighed accurately) was extracted by 100 cc. of acetone for 48 hours[12]; the acetone was evaporated on a water-bath; the residue was dried for 2 hours in an oven at 90° C; the dry acetone extract was taken up in 100 cc. of chloroform; the filtered solution was evaporated on the water-bath, and finally dried for 2 hours in the oven at 90° C.

In the subsequent determination, it was necessary to know the precise weight of the portion soluble in chloroform. Knowing this weight, a sample is taken, put in solution in chloroform, and brought to the concentration of 0.4 gram per liter (the concentration at which the spectrum of this solution is most characteristic and offers the best possibility of its successful determination).

The spectrum of this solution was compared with that of zinc dimethyldithiocarbamate at a concentration of 0.2 gram per liter.

Study of the range within which a determination is possible.

The difference in concentration between the solution of the sample (0.4 gram per liter) and that of the standard control solution for comparison (0.2 gram per liter) made it possible to reach a first approximation in studying the extent of the transformation.

To obtain more precise results, it was necessary, as was pointed out in earlier work on the determination of antioxygenic substances, to determine the range of the spectrum within which the rubber resins have no influence on the true absorption due to zinc dimethyldithiocarbamate.

By comparing the spectrum of a solution of pure zinc dimethyldithiocarbamate (concentration of 0.2 gram per liter) with that of a solution which contains the same concentration of zinc dimethyldithiocarbamate but is augmented by 0.4 gram of rubber resins per liter, it was found that the resins had no effect around 2850 Å.U. It is in this region, therefore, that the measurements had to be made.

Results obtained.

A large number of acetone extractions were made, and the zinc dimethyldithiocarbamate in the extracts was found to lie between 2.80 and 3.10 grams per 100 grams of rubber, *i.e.*, 105 grams of the rubber mixture. These values correspond to 2.1 and 2.3 grams, respectively, of tetramethylthiuram disulfide. Since the quantity added was 3 grams, the recovery in this way was 70 to 76 per cent of the original disulfide.

Figure 4 shows a representative spectrographic determination.

VERIFICATION OF THE EXACT NATURE OF THE PRODUCT ANALYZED SPECTROGRAPHICALLY

To verify the fact that the compound determined by the spectrographic method actually was zinc dimethyldithiocarbamate, it was necessary: (1) to isolate this zinc dimethyldithiocarbamate, and then (2) to identify it by chemical means.

To confirm the results, a balance sheet of sulfur can then be made, in which account is taken of all tetramethylthiram disulfide not transformed into zinc dimethyldithiocarbamate, and which will thereby make it possible to check the accuracy of all the determinations.

Separation of zinc dimethyldithiocarbamate in the acetone extract of the vulcanized mixture.

The low solubility of zinc dimethyldithiocarbamate may be a troublesome factor in certain manipulations; on the other hand it becomes an advantage when it is desired to isolate it. As a matter of fact the rubber resins are actually amino acids (decomposition products of the proteins) and fat acids which are very soluble in absolute alcohol, whereas zinc dimethyldithiocarbamate is very little soluble. By washing the acetone extract with cold absolute alcohol, a good separation is obtained, without too great loss of zinc dimethyldithiocarbamate. The actual operation is first to deresinify the dry extract by washing it repeatedly with several cc. of acetone until the acetone is clear; to filter the powdery residue, and to extract the filter in a Soxhlet apparatus with alcohol for 10 hours. This last operation eliminates, in addition to the

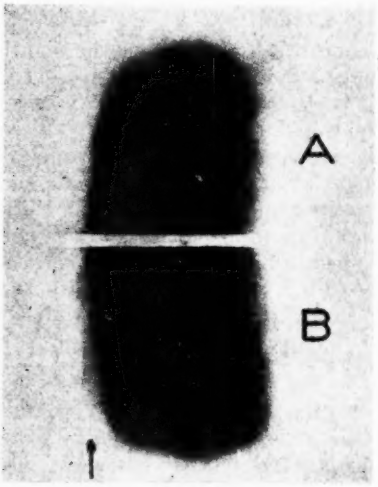


FIG. 4.—Example of a determination of zinc dimethyldithiocarbamate in a mixture vulcanized with tetramethylthiuram disulfide.
A. Spectrum of the acetone extract of the mixture (concentration 0.4 gram per l.).
B. Spectrum of pure zinc dimethyldithiocarbamate (concentration 0.1 gram per l.).
The arrow indicates the location where the measurements were made, *viz.*, at about 2.850 A.U.

resins, any traces of tetramethylthiuram monosulfide and disulfide which might have been entrained.

In this way a product is obtained which is not white like zinc dimethyldithiocarbamate, but is brown. The yield of zinc dimethyldithiocarbamate was 4.8 grams, a value which indicates that 60 per cent of the tetramethylthiuram disulfide was transformed. This value, obtained by gravimetric determination, is fairly close to that found spectrographically, but nevertheless is slightly lower.

This difference is attributable first to the washing with alcohol, but above all else to the fact that in spectrographic determinations it is possible to operate with very small quantities of rubber, *i.e.*, of the order of 1 gram, and under such conditions extraction is relatively easy. On the contrary, in a gravimetric determination, to obtain a quantity of zinc dimethyldithiocarbamate sufficient for subsequent confirmatory tests, 80 grams of the rubber mixture was extracted

for 1 week[14]. But in spite of this relatively long time, this large quantity of rubber mixture made complete extraction impossible, and a certain amount of zinc dimethyldithiocarbamate remained in the rubber. Actually a determination of the sulfur remaining in the extracted rubber mixture showed 0.40 per cent (based on the rubber itself). Actually the limiting value of unextractable sulfur in the rubber mixture used is 0.35 per cent. This corresponds to the complete separation of zinc dimethyldithiocarbamate, which can be readily attained in extractions of the small quantities of material used in spectrographic determinations.

Chemical identification of zinc dimethyldithiocarbamate extracted from rubber.

After having succeeded in extracting zinc dimethyldithiocarbamate from rubber, the remaining problem was to identify it. The melting points of the product alone and when mixed with the pure compound are in themselves a good indication. A melting point of 246–247° C was found in each case, which is the melting point of pure zinc dimethyldithiocarbamate. This preliminary identification was confirmed by stoichiometric determinations of the percentages of sulfur, zinc, and nitrogen.

The determination of nitrogen offered no particular difficulty. An apparatus of the Parnas and Wagner type for the semimicrodetermination of nitrogen by the Kjeldhal method was available and was used for the determinations.

On the other hand the determinations of sulfur and zinc were more delicate. In the case of sulfur, where it is necessary to avoid the formation of volatile carbon disulfide, recourse was had to the method of Delépine[15], whereby the sample is oxidized by potassium manganite and the potassium sulfate formed is determined in the usual way.

To determine zinc, the volumetric method of von Grote[16] was used. Zinc dimethyldithiocarbamate is easily decomposed by acids, and by treating it with hydrochloric acid, the zinc passes into solution as zinc chloride. It is then determined with potassium ferrocyanide, with uranyl acetate or ammonium molybdate as indicator.

Examination of the extracted zinc dimethyldithiocarbamate showed that it was crystalline. In boiling acetone for several hours, pure zinc dimethyldithiocarbamate was transformed into a crystalline form identical in every way to the crystals extracted from rubber. These are shown as photomicrographs in Figure 2. These crystals were also analyzed, with the results shown in the accompanying table.

ZINC DIMETHYLDITHIOCARBAMATE

	Theoretical	Pure	Extracted from rubber	Crystallized from boiling acetone
Sulfur	41.91	41.96–42.05	41.91–42.17	42.41–42.05
Zinc	21.35	21.55–21.17	21.53–21.42	21.77–21.76
Nitrogen	9.15	9.36– 9.45	9.08– 9.06	9.24– 9.26
Melting point	—	247° C	247° C	247° C
Color		white	brown	brown

Investigation of what becomes of that part of the tetramethylthiuram disulfide which is not transformed into zinc dimethyldithiocarbamate.

By making a balance sheet of sulfur, it is possible to evaluate both the spectrographic and the gravimetric determinations.

The extracted rubber still contains a certain quantity of sulfur (at least 0.35 per cent based on the rubber), which evidently comes from the tetra-

methylthiuram disulfide. Consequently not all of this accelerator can be recovered in the form of zinc dimethyldithiocarbamate. The sulfur of tetramethylthiuram disulfide is composed of two parts: (1) that which is transformed into zinc dimethyldithiocarbamate, and (2) that which remains in the extracted rubber. This second part (0.35 per cent) represents a quantity of tetramethylthiuram disulfide equivalent to 0.65 per cent of the rubber. By adding to this value that corresponding to the part transformed into zinc dimethyldithiocarbamate, *i.e.*, 2.1 to 2.3 grams, a value corresponding to 2.75 to 2.95 grams of tetramethylthiuram disulfide is obtained.

The agreement is sufficiently good to confirm the value obtained in the determinations, and it shows also that the last one-third of the tetramethylthiuram disulfide, which is not transformed into zinc dimethyldithiocarbamate, must either combine with the rubber or be decomposed, but in any event does not form tetramethylthiuram monosulfide.

STUDY OF THE EFFECTS OF THE PROLONGED ACTION OF HOT ACETONE ON THE RUBBER MIXTURE

In view of the fact that Maximoff[10] has shown that it is possible to obtain zinc dimethyldithiocarbamate by the direct action, at 147° C, of tetramethylthiuram disulfide on zinc oxide, it was essential to study the effects of the extraction resulting from the prolonged action of boiling acetone in order to ascertain whether or not it is sufficient to bring about the formation, even if only partial, of the zinc dimethyldithiocarbamate which is found in the rubber.

Tetramethylthiuram disulfide alone.

A solution of tetramethylthiuram disulfide in acetone, even when saturated, is a clear yellow color. On the contrary, when several grams of tetramethylthiuram disulfide is extracted with acetone, the resulting extract becomes brown in a few hours, then dark brown, and finally almost black. Evidently some sort of transformation takes place. Spectrographic examination shows, moreover, that a new compound has been formed. An indication of the nature of the transformations which are observed can be had from the experiment to be described. When, rather than tetramethylthiuram disulfide, tetramethylthiuram monosulfide and tetrasulfide are extracted with acetone, their behavior is very different. Under the same conditions as for the disulfide, the monosulfide is not changed; on the contrary, the tetrasulfide, an acetone solution of which is normally clear, gives a liquid which rapidly turns so dark brown that it appears almost black. This change in color, which, is mentioned, does not take place in the case of the monosulfide, is much more pronounced in the case of the tetrasulfide than it is in the case of the disulfide. When the acetone extraction is made, not of the monosulfide alone, but of a mixture of monosulfide and a quantity of sulfur exactly that necessary to make the disulfide, the same phenomenon of color change as with the disulfide is found to take place.

These results make it probable that a reaction takes place in which acetone plays an important part, for there is no such reaction in benzene, and they also point to a highly unstable condition of the molecules of the disulfide and tetrasulfide.

Whatever the explanation of the phenomena, tetramethylthiuram disulfide is affected by extraction with acetone. Since the phenomenon is of only indirect interest in the present problem, no further investigation was made to determine what sort of transformation takes place nor the extent of this change.

Mixture of tetramethylthiuram disulfide and zinc oxide.

Spectrographic examination of the residue of the extraction of a mixture of tetramethylthiuram disulfide and zinc oxide showed that zinc dimethyldithiocarbamate is formed to the extent of about 5 per cent.

Mixture of rubber, tetramethylthiuram disulfide and zinc oxide (unvulcanized).

It might be thought that it would be difficult to distinguish between the transformations brought about by vulcanization and those resulting from acetone extraction. Unfortunately, however, when a mixture, not merely of tetramethylthiuram disulfide and zinc oxide, but a mixture of these two powders incorporated into unvulcanized rubber, is extracted with acetone, the same result is obtained as in the case of extraction of tetramethylthiuram disulfide alone. No zinc dimethyldithiocarbamate is formed. It may, therefore, be concluded that the unidentified compound formed in the extract of the vulcanized mixture is formed exclusively during vulcanization and not during extraction.

INFLUENCE OF RUBBER RESINS AND PROTEINS ON THE TRANSFORMATION OF TETRAMETHYLTHIURAM DISULFIDE

It seemed of interest to determine whether deresinified rubber and deproteinized rubber vulcanize under the same conditions as untreated rubber, and whether decomposition of tetramethylthiuram disulfide takes place in these cases in the same way, with formation of zinc dimethyldithiocarbamate. It is conceivable that the rubber proteins are responsible for vulcanization and particularly for the transformation of tetramethylthiuram disulfide into zinc dimethyldithiocarbamate by furnishing hydrogen to combine with the oxygen of zinc oxide.

Deproteinized rubber containing less than 0.02 per cent of nitrogen was vulcanized to test this hypothesis. The result was the same as obtained with rubber which had not been deproteinized as well as with rubber previously extracted with acetone. This seems to indicate that neither proteins nor fat acids play any part in the transformation of tetramethylthiuram disulfide into zinc dimethyldithiocarbamate.

VULCANIZATION BY TETRAMETHYLTHIURAM MONOSULFIDE

In the absence of sulfur, tetramethylthiuram monosulfide is not capable of bringing about vulcanization[17]. On the contrary the addition to it of an amount of sulfur corresponding to the formation of tetramethylthiuram disulfide is sufficient to bring about vulcanization. With any other accelerator this quantity of sulfur would not be sufficient, yet with tetramethylthiuram monosulfide it is not all consumed in combining with the rubber, for after vulcanization zinc dimethyldithiocarbamate is found to be present and the formation of this form tetramethylthiuram monosulfide requires the addition of sulfur.

As an example, the following mixture:

Rubber	100
Sulfur	0.47
Tetramethylthiuram monosulfide	3
Zinc oxide	2

was vulcanized 30 minutes at 125° C. The vulcanizate had a tensile strength of 150 kg. per sq. cm.

The proportion of sulfur which could not be extracted by acetone was similar to that which was found in the rubber-tetramethylthiuram disulfide mixture, *i.e.*, of the order of 0.4 per cent, and the acetone extract contained 2.25 per cent of zinc dimethyldithiocarbamate (based on the rubber).

If it is assumed that one molecule of tetramethylthiuram monosulfide forms one molecule of zinc dimethyldithiocarbamate, this corresponds to more than 60 per cent of the monosulfide transformed in this way.

A comparison of this result with that observed when tetramethylthiuram monosulfide and disulfide are heated, with and without sulfur, in acetone, makes it seem probable that there is a relation between the possibility of scission of tetramethylthiuram disulfide molecule in its center and the possibility of vulcanization.

EXAMINATION OF PREVIOUS WORK ON VULCANIZATION BY TETRAMETHYLTHIURAM DISULFIDE

According to what has just been described in this work, it appears that the generally accepted theories regarding vulcanization by tetramethylthiuram disulfide are not valid after all, and that more value is lent to the experiments of Shepard[8] and of Shimada[9], which have in the past received no attention. These investigators, basing their work on color reactions, have shown that it is possible to detect the presence of zinc dimethyldithiocarbamate in vulcanizates cured with tetramethylthiuram disulfide.

The work of Shepard appeared in 1934 in the form of a short note in which the author described experiments in which a vulcanizate prepared from a mixture of crepe rubber 100, tetramethylthiuram disulfide 3, and zinc oxide 2, was immersed in a saturated solution of cupric sulfate or cobalt nitrate. The surface of the mixture became colored, and the color thus acquired by the surface depended on the reagent, *e.g.*, with cupric sulfate solution it became red, and with cobalt nitrate it became green. Since cupric dimethyldithiocarbamate is red and cobalt dimethyldithiocarbamate is green, Shepard concluded that zinc dimethyldithiocarbamate is present in rubber vulcanized by tetramethylthiuram disulfide.

It seemed advisable to repeat this experiment, using ultraviolet absorption spectra. The same mixture as that used by Shepard was immersed in a saturated solution of cupric sulfate and in a saturated solution of cobalt nitrate. In cupric sulfate solution the reaction was very sharp and rapid; the solution changed from dark blue to pale blue, an indication that copper ions were absorbed. The rubber mixture, which was light yellow, became covered with a brown coating. All these changes took place in less than one hour.

In cobalt nitrate solution the action was much less well defined; nevertheless, at the end of a day, the mixture became covered with a green coating, without any change in the color of the solution.

The mixtures were washed with water, then with chloroform. The chloroform wash liquors showed a characteristic absorption in the ultraviolet region analogous to the absorption exhibited by cupric dimethyldithiocarbamate and by cobalt dimethyldithiocarbamate. The most well defined spectrum was obtained with copper, as is shown in Figure 5.

The work of Shimada[9] is more recent. This investigator carried out a great deal of work on color reactions of accelerators and antioxygenic substances.

One of the reagents with which he obtained the best results was cobalt oleate. He showed that with this reagent tetramethylthiuram disulfide does not give any color reaction, whereas the acetone extract of rubber vulcanized by tetramethylthiuram disulfide gives a green color reaction. Now this green color is the same as that obtained when cobalt oleate and zinc dimethyldithiocarbamate react. Since the principle of this test is the same as that described by Shepard[8], it was not considered worthwhile to repeat the experiment. The same remarks apply to two other cases in which cobalt salts other than the dimethyldithiocarbamate give green colorations.

According to Maximoff[10], when tetramethylthiuram disulfide reacts directly with zinc oxide, with no solvent present, zinc dimethyldithiocarbamate is also formed. This experiment was repeated by the present author by heating a mixture of 3 parts of tetramethylthiuram disulfide with 2 parts of zinc oxide for 2 hours at 147° C. The product was at first gray, but melted, turned to orange,

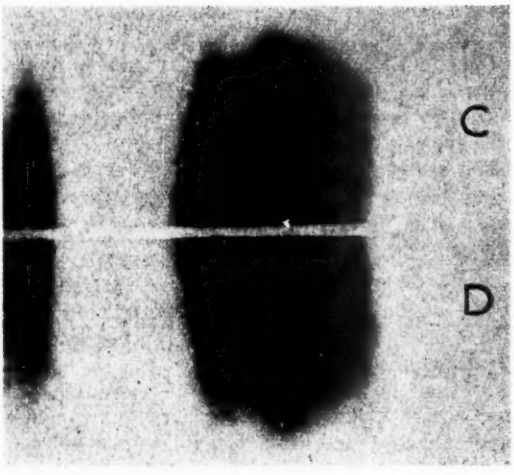


FIG. 5.

C. Spectrum of the solution from washing the mixture after immersion in a copper sulfate solution.
D. Spectrum of copper dimethyldithiocarbamate (concentration 0.1 gram per l.).

and lost 5.5 per cent of its weight. It was found that 60 per cent of the tetramethylthiuram disulfide was transformed into zinc dimethyldithiocarbamate. This determination was made by the spectrographic method, and zinc dimethyldithiocarbamate also was isolated by taking advantage of its low solubility in alcohol.

With a view to studying this transformation more thoroughly, further experiments were carried out, in which the influence of temperature was first investigated. The same mixture as that given above was heated for 2 hours at 100°, 120°, 130° and 140° C, respectively. At the highest temperature zinc dimethyldithiocarbamate was still formed at 147° C as described above, but at 130° C only traces were identified, and at 120° C there was no transformation even after heating for 8 hours.

The influence of the surrounding atmosphere was then examined. Heating in a vacuum, in air, and in a current of pure dry hydrogen gave identical results. On the contrary heating in a current of hydrogen sulfide promoted considerably

the formation of zinc dimethyldithiocarbamate. The rate of passage of hydrogen sulfide (which was controlled at 8.20 liters per hour) and the proportion of tetramethylthiuram disulfide to zinc oxide had an influence on the course of the reaction. The powders, in a flask, became orange and formed a sort of paste. Spectrographic analysis showed that a period of heating of 8 hours at 100° C in hydrogen sulfide resulted in a transformation of the order of 40 per cent into zinc dimethyldithiocarbamate.

Finally experiments were, of course, carried out to determine whether, under the conditions used in vulcanizing the mixture as already described, any zinc dimethyldithiocarbamate is formed. In this experiment the time and temperature actually used in vulcanizing the rubber mixture was used, *viz.*, 30 minutes at 125° C. When a mixture of the two powders was heated under these conditions, no zinc dimethyldithiocarbamate was formed.

As a result of all these experiments, two particularly important facts emerge. First of all, it is not possible, by the direct action of zinc oxide on tetramethylthiuram disulfide, to obtain any zinc dimethyldithiocarbamate under the conditions in which vulcanization was carried out. Secondly, if instead of operating under the conditions used in vulcanizing the rubber mixture, a higher temperature approaching that of the melting point of tetramethylthiuram disulfide is used, transformation of the latter into zinc dimethyldithiocarbamate actually does take place.

In view of this, it seems probable that the hydrogen necessary to remove the oxygen from the zinc oxide according to the reaction:

$$(H_3C)_2NC(:S)SSC(:S)N(CH_3)_2 + ZnO + H_2 \longrightarrow (H_3C)_2NC(:S)SZnSC(:S)N(CH_3)_2 + H_2O,$$

comes from decomposition products of tetramethylthiuram disulfide. However, the presence of a donor of hydrogen, *e.g.*, hydrogen sulfide, promotes and accelerates the transformation.

Instead of following what happens when the reaction is carried out by heating in a gaseous medium, it is possible to carry out the reaction in a liquid. Grenness[4] in particular has described the formation of zinc dimethyldithiocarbamate by simply heating tetramethylthiuram disulfide and active zinc oxide[18] in benzene.

If dehydrogenation is at the expense of benzene, it should be possible to recover biphenyl as a product of the reaction.

$$(H_3C)_2NC(:S)SSC(:S)N(CH_3)_2 + ZnO + 2C_6H_6 \longrightarrow (H_3C)_2NC(:S)SZnSC(:S)N(CH_3)_2 + H_5C_6 \cdot C_6H_5 + H_2O.$$

But in spite of the formation of zinc dimethyldithiocarbamate having been verified under the conditions used by Grenness, no biphenyl could be detected under the same conditions, although a control experiment showed that it would be very easy to identify as little as 1 per cent of the theoretical yield formed by the reaction above. In order to leave no doubt at all as to the presence of zinc dimethyldithiocarbamate, the experiments of Grenness were completed by isolating and weighing the zinc dimethyldithiocarbamate which was formed. A mixture of 50 grams of active zinc oxide and 4 grams tetramethylthiuram disulfide was heated for 20 hours at 80° C in 500 cc. of benzene. After filtration, the benzene was yellow. It was distilled in a rectifying column, and it passed over completely at 80° C. The residue in the flask was a cream-colored powder (2.597 grams), the melting point of which was 244–245° C. Zinc oxide itself

was extracted with acetone, and yielded 1.567 grams of a powder which melted at 244–245° C. There was, then, a total of 4.173 grams of impure zinc dimethyldithiocarbamate. Since the impurity is tetramethylthiuram disulfide and this is very soluble in alcohol, whereas zinc dimethyldithiocarbamate is only slightly soluble, the product was washed in a Soxhlet with absolute alcohol for 3 hours. The powdery residue had a melting point of 246–247° C, both alone and when mixed with pure zinc dimethyldithiocarbamate. The yield was 3.24 grams, which indicates a yield above 75 per cent, for the washing with alcohol unquestionably carried away a little zinc dimethyldithiocarbamate[19].

Since no dehydrogenation product of benzene was found, and since the yield from the transformation was high, it must be concluded that, in this case, the hydrogen necessary for the reaction probably originates from the tetramethylthiuram disulfide itself or from the zinc oxide. As a matter of fact, active zinc oxide is not a pure product, and the zinc oxide used in the experiments had the following characteristics.

	Technical zinc oxide used for vulcanization	Active zinc oxide
Acidity in H_2SO_4 (with phthalein)	0.36%	0.006%
pH value (dispersed in distilled water)	7.15	9.32
Sulfur	0.23%	1.21%
Carbon dioxide	0.024%	2.85%
Lead	none	none
Magnesium oxide	none	0.50%
Chlorine	none	0.04%
Zinc	none	1.90%
Zinc oxide	98.7%	83%
Particle size	90% = 3μ	colloidal

Although active zinc oxide is currently used only to a limited extent, it was necessary to study its behavior, not only as a means of checking the results obtained by Grenness, but also, and this is very important, because it has such a peculiar action in contrast to the zinc oxide used in the present work, which was of the type used generally by the rubber industry and which was found to be incapable of forming zinc dimethyldithiocarbamate under the same conditions.

It is well, however, to compare these phenomena with what was found when acetone was used. When the reaction is carried out in acetone rather than in benzene, ordinary zinc oxide gives small yields of zinc dimethyldithiocarbamate. But here again, perhaps because the quantity formed is too small, it has not been possible to obtain any indication of the formation of the dehydrogenation product of acetone, *viz.*, acetonylacetone. On the contrary, just as with reactions in gaseous media, the presence of a donor of hydrogen (hydrogen sulfide) promotes the transformation of tetramethylthiuram disulfide into zinc dimethyldithiocarbamate, both in acetone solution and in benzene solution, and the latter solution even induces the reaction to take place with ordinary zinc oxide.

CONCLUSIONS

Various experiments make it clear that the method of spectrographic determination can be applied to a complicated case where the product to be determined does not remain intact in a mixture but is transformed into some other compound.

Furthermore the results obtained, which were confirmed by chemical tests, are definite and precise enough to make it possible to determine the type of transformation which takes place in rubber when tetramethylthiuram disulfide is used as a vulcanizing agent. The liberation of sulfur is only an accessory reaction, in fact there is probably not even any such reaction. More probably there is a dehydrogenation of the rubber, without liberation of hydrogen sulfide, a dehydrogenation which involves perhaps certain restricted parts of the molecule, *e.g.*, the extremities of the chains, as has been suggested by Boggs and Blake[20].

It is possible to conceive various schemes whereby this dehydrogenation may take place and which would make it possible to explain at the same time the formation of zinc dimethyldithiocarbamate, the decrease in unsaturation found by Hauser and Brown[11], and the fixation of a certain amount of sulfur on the rubber.

REFERENCES

[1] Bruni, *India-Rubber J.* **62**, 89 (1921).
[2] Cummings and Simmons, *Ind. Eng. Chem.* **20**, 1173 (1928).
[3] Twiss, Brazier and Thomas, *J. Soc. Chem. Ind.* **41**, 81T (1922).
[4] Grenness, "The Accelerated Vulcanization of Rubber", London, **1937**.
[5] For the complete details of ultraviolet spectrography and the operating methods, see earlier publications of Dufraisse and Houpillart (*Rev. Opt. Thér. Instr.* **16**, 321 (1937); *Rev. gén. caoutchouc* **16**, 44 (1939), and the Thesis of Jarrijon (Thesis, Paris, **1942**).
[6] Under certain conditions, *e.g.*, with rubber extracted with acetone, traces of tetramethylthiuram monosulfide were detected.
[7] Dufraisse and Jarrijon, *Compt. rend.* **215**, 181 (1942); *Rev. gén. caoutchouc* **20**, 74 (1943).
[8] Shepard, *Ind. Eng. Chem.* **26**, 1200 (1934).
[9] Shimada, RUBBER CHEM. TECH. **11**, 535 (1938).
[10] Maximoff, *Caoutchouc & gutta-percha* **18**, 10944 (1921).
[11] Hauser and Brown, *Ind. Eng. Chem.* **31**, 1226 (1939).
[12] Even after extraction for 48 hours, sulfur was still found in the extracted rubber. Part of the accelerator or of its decomposition products still remained in the mixture. It was found that still more prolonged extraction did not reduce this quantity.
[13] Jarrijon, *Rev. gén. caoutchouc* **18**, 217 (1941).
[14] This extraction was carried out in an apparatus of the Soxhlet type, and in the cold.
[15] Delépine, *Bull. soc. chim.* **8**, 685 (1941).
[16] Von Grote, *Angew. Chem.* **54**, 539 (1941).
[17] After heating the mixture for 30 minutes at 125° C, almost all the monosulfide was recovered. Only a very small quantity of zinc dimethyldithiocarbamate, i.e., less than 10 per cent, was formed. This represents an incipient vulcanization, and it is attributable to impurities in the monosulfide, which is difficult to purify and which, because of its not being perfectly stable, may contain traces of sulfur.
[18] It is known that ordinary types of zinc oxide are obtained by heating the fused metal. In this way pigments having a density of approximately 5.6 are obtained. Active types of zinc oxide are complex colloidal products, the purity of which is not necessarily 100 per cent. As obtained usually in the wet way and dried under special conditions, they are colloidal and ultradispersed. Their apparent density is 0.1–0.15. It has even been claimed that their fineness is of the molecular order.
[19] Based on a simple iodine determination, Grenness (see Reference 4) reported a yield of 57 per cent.
[20] Boggs and Blake, *Ind. Eng. Chem.* **22**, 748 (1930).

SPECTROPHOTOMETRIC DETERMINATION OF THE STYRENE CONTENT OF BUTADIENE-STYRENE COPOLYMERS *

E. J. MEEHAN

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS

Smakula[1] has measured the ultraviolet absorption spectra of polystyrene samples, the molecular weights of which varied between 3900 and 240,000. He found that the absorption curves were of the same form for the seven polystyrene samples which he studied, regardless of the molecular weight of the sample, and that the molar absorption coefficient at the absorption maximum (260 mμ) was directly proportional to molecular weight. He showed that the absorption spectrum of polystyrene is entirely different from that of monostyrene, but is the same as that of ethyl benzene; even the absorption coefficient at the absorption maximum is the same, within 10 per cent, as the absorption coefficient of ethyl benzene, if the comparison is made on the basis of the number of benzene rings present in each substance. These facts led Smakula to the following conclusions: (1) absorption of light by polystyrene in the near ultraviolet (about 260 mμ) is due to the presence of benzene rings (phenyl residues), rather than to a residual ethylenic linkage, and (2) there is virtually no interaction between the benzene rings (nonconjugated system). These conclusions are in agreement with the accepted structure of polystyrene.

Since the molar absorption coefficient of polystyrene at 260 mμ is directly proportional to the molecular weight of the polymer, the specific extinction coefficient, referred to weight concentration of polystyrene, is constant (independent of molecular weight). Spectrophotometric measurements do not make possible the determination of the molecular weight of a polystyrene sample, but they do permit the determination of the weight concentration of polystyrene in an unknown solution. Such a concentration determination can be carried out in the presence of other components of the solution which absorb light of the same wave length, if a correction can be made for the absorption due to these components.

The results of Smakula previously referred to, and consideration of the structure of copolymers of styrene with, *e.g.*, butadiene, lead to the conclusion that the phenyl residues in a butadiene-styrene copolymer act independently with regard to the absorption of light, just as they do in polystyrene. Evidently then, the problem of determining the fraction of a butadiene-styrene copolymer which is styrene is formally analogous to the problem of determining the weight of concentration of polystyrene in an unknown solution. This determination can be carried out by spectrophotometric means.

This possibility was first realized experimentally by Hulse, Hart, French, and Matheson[2]. These workers were the first to show that the absorption spectrum of GR-S, a butadiene-styrene copolymer, is similar in detail to that of polystyrene, so that a determination of absorption intensity makes possible the calculation of the chemical composition of the copolymer.

* Reprinted from the *Journal of Polymer Science*, Vol. 1, No. 3, pages 175–182, May 1946.

EXPERIMENTAL

Preparation of Polymers and Copolymers.—Various samples of polystyrene, polybutadiene, and butadiene-styrene copolymer were prepared by emulsion polymerization. Polystyrene was prepared according to Kolthoff and Dale[3].

	Parts by wt.
Styrene	100
Water	180
Potassium persulfate	0.3
n-Dodecyl mercaptan	0.5
Soap (Ivory Flakes)	5.0

Polybutadiene and the butadiene-styrene copolymers were prepared according to the same formulation, with all or part of the styrene substituted by an equal weight of butadiene. The polymerizations were carried out for various lengths of time at 50° C. The butadiene (Carbide and Carbon Chemicals Corporation) was over 99 per cent pure; it was bubbled through sodium hydroxide and condensed in a dry ice-acetone mixture before use. The styrene (Monsanto) was at least 99.5 per cent pure, and contained a trace of inhibitor; it was used without further purification, since preliminary tests had shown that the same results were obtained whether or not the styrene was first purified by careful distillation. After polymerization had proceeded for the desired length of time, the polymerization reaction was halted by the addition of a trace of hydroquinone or β-naphthol. The polymer was obtained from the latex by addition of the latex to ethanol with stirring; the polymer was washed several times with ethanol and dried in a vacuum oven. In a few instances, the polymer was subjected to ethanol extraction in a Soxhlet apparatus. Extraction did not affect the absorption spectrum, thus indicating that the polymer must have been practically pure before the extraction was carried out. It should be noted, however, that careful purification is necessary if the spectrophotometric method herein described is applied to copolymers produced on a commercial scale, since such copolymers generally contain appreciable quantities of substances which absorb strongly in the near ultraviolet.

Spectrophotometric Measurements.—All spectrophotometric measurements were made with a Beckman ultraviolet spectrophotometer, using 1.000 cm. silica cells. The measurements were made with a slit width of 0.50 mm., which corresponds to a band width of 1.3 mμ at 260 mμ. The polymers were dissolved in chloroform. The results are expressed in terms of the specific extinction coefficient, E^*, at a given wave length. E^* is defined in the usual way as the measured extinction (read directly on the spectrophotometer), divided by concentration in grams per liter (1 cm. cells).

RESULTS

Spectrum of Polystyrene.—Six samples of polystyrene were prepared by emulsion polymerization, with the percentage conversion of monomer to polymer ranging from about 30 to almost 100 per cent. These polymers are known to be heterogeneous with respect to molecular weight, and those of high conversion presumably contain relatively more high molecular weight material than those of low conversion. In agreement with the results of Smakula, it was found that the shape of the near ultraviolet absorption curve and the value of the specific extinction coefficient, E^*, were the same for all the polystyrene samples. The values of E^* at 262.0 mμ (wave length of maximum absorption)

were 2.14, 2.04, 2.10, 2.10, 2.13, 2.27, and 2.26. The average value is 2.16 ± 0.07 (average deviation of 3.5 per cent). The absorption curve of polystyrene is shown in Figure 1*a*.

Spectrum of Polybutadiene.—Four samples of polybutadiene were prepared by emulsion polymerization, with the conversion of monomer to polymer ranging from 9 to 86 per cent. (This range of conversion corresponds to the change from a soft, low-molecular weight material to a hard, elastic, high-molecular weight material.) Measurements were made on chloroform solutions in the region 250–300 mμ, in which region polybutadiene exhibits only relatively weak absorption with no absorption maximum (Figure 1*b*). The intensity of absorption is practically independent of the degree of conversion, and, therefore, of the average molecular weight, as is shown by the data of Table I.

TABLE I

SPECIFIC EXTINCTION COEFFICIENT OF POLYBUTADIENE IN CHLOROFORM AT 262.0 Mμ

Per cent conversion of monomer to polymer	Specific extinction coefficient
9	0.040
25	0.036
55	0.039
86	0.055
	Average 0.042

The value of the specific extinction coefficient of polystyrene at 262 mμ is more than fifty times as great as that of polybutadiene at the same wave length.

An analysis of the absorption curves of the various polybutadiene samples shows that the extinction values are the same throughout this region. The relative values of E^*, that at 262.0 mμ being taken as unity, are given in Table II.

TABLE II

VALUES OF SPECIFIC EXTINCTION OF SAMPLES OF POLYBUTADIENE OF VARIOUS DEGREES OF POLYMERIZATION, RELATIVE TO THE VALUES AT 262.0 Mμ

Wave length, mμ	9%	25%	55%	86%	Average
250	2.01	2.15	2.04	1.89	2.02
260	1.09	1.09	1.08	1.08	1.09
270	0.78	0.81	0.82	0.79	0.80
280	0.66	0.71	0.72	0.70	0.70
290	0.56	0.58	0.60	0.58	0.58
300	0.45	0.44	0.47	0.45	0.45

Spectrum of Butadiene-Styrene Copolymer.—Butadiene-styrene copolymers were prepared in emulsion with various proportions of butadiene and styrene in the charge, and at various conversions of monomers to polymer. The absorption spectrum of a copolymer made with 75 per cent butadiene and 25 per cent styrene (by weight) in the charge, polymerized to about 10 per cent yield of polymer, is shown in Figure 1*c*.

CALCULATION OF STYRENE CONTENT OF THE COPOLYMER

If the copolymer is made up of two substances, styrene and butadiene, which act independently with regard to the absorption of light, and which follow Beer's law, it is clear that:

$$E^* = xE_S^* + (1 - x)E_B^* \qquad (1)$$

in which E^* = specific extinction coefficient of the copolymer at a given wave length, E_S^* and E_B^* = specific extinction coefficients of pure polystyrene and pure polybutadiene, respectively, and x = fraction of the copolymer which is styrene. The equation may be arranged to give:

$$x = (E^* - E_B^*)/(E_S^* - E_B^*) \qquad (2)$$

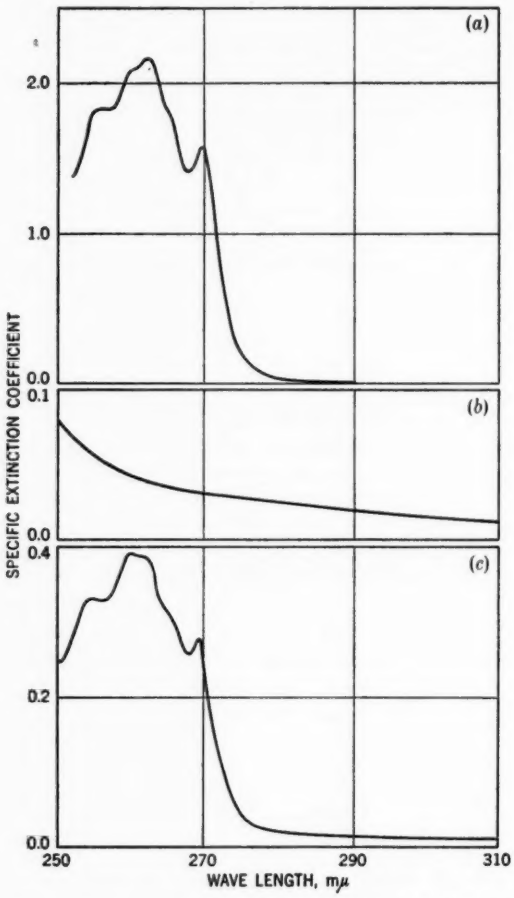


FIG. 1.—Absorption spectra of (*a*) polystyrene, (*b*) polybutadiene, and (*c*) butadiene-styrene copolymer.

In Equation (1) it is assumed that the only copolymer constituents are styrene and butadiene. The effect of other constituents which have relatively very weak light absorption could obviously be corrected for arithmetically. Impurities which are strongly light absorbing, however, must be removed.

Spectrophotometric measurements on copolymers of accurately known composition would provide an experimental test of Equation (2). Direct absolute chemical analysis (*i.e.*, an analysis based on stoichiometric relations alone) of butadiene-styrene copolymer can be made only by determination of

the carbon-hydrogen ratio by combustion analysis[4]. Because of the close similarity in the elementary compositions of butadiene (88.8 per cent carbon) and styrene (92.3 per cent carbon), the determinations must be unusually accurate (as distinguished from precise) if significant results are to be obtained for the composition of the copolymer.

One way to obtain polymers of known composition is to allow the polymerization reaction to go almost to completion, because, although the composition of the copolymer varies during the reaction in a manner which cannot be assumed *a priori*, the overall composition of the copolymer at 100 per cent conversion of the monomers necessarily is the same as the composition of the

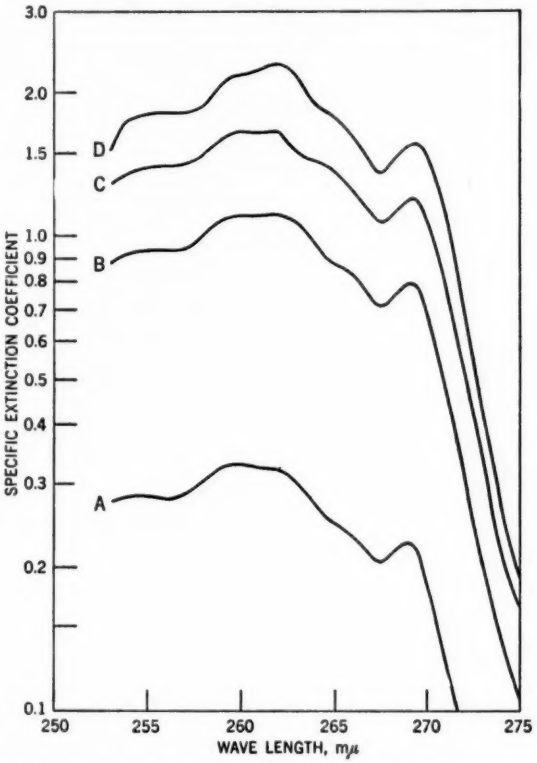


FIG. 2.—Absorption spectra of butadiene-styrene copolymers: A, 12.5% styrene; B, 50% styrene; C, 75% styrene; D, polystyrene.

monomers used in the preparation. (In butadiene-containing copolymers, the polymer becomes partially insoluble in chloroform before 100 per cent conversion is attained, so that the conversion cannot be carried quite so far.) This procedure has been used to obtain copolymers of approximately (but not exactly) known composition for a test of Equation (2). Three polymers were prepared with 12.5, 50, and 75 per cent (by weight) styrene in the charge. The polymerization times were so chosen that the conversions were almost 100 per cent. The absorption curves are shown in Figure 2, which also includes that of polystyrene. E^* is plotted against x (the fraction of the copolymer which is styrene) for various wave lengths, in Figure 3. This figure shows that

the assumptions embodied in Equation (2) are approximately correct, within the limits of reproducibility of the preparation of the copolymers[5].

Examination of the curves of Figure 2, however, reveals that the assumption of simple additivity of the absorption spectra of polystyrene and polybutadiene to produce that of the copolymer is not exact. This is shown by the shift of the wave length of maximum absorption, with decreasing styrene content, from 262.0 to 260.0 mμ. Calculations show that this shift is larger than can be accounted for by the superposition of the two spectra. The existence of such an effect is not surprising, however, for the copolymer actually is a chemical compound of styrene and butadiene rather than a mixture of polystyrene and polybutadiene. Indeed the slight perturbation in the absorption spectrum may be regarded as (qualitative) spectroscopic evidence that the copolymer actually is a chemical compound.

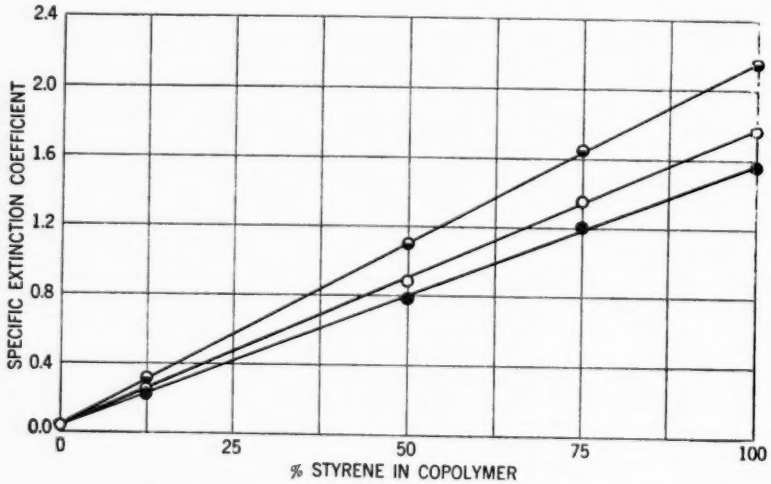


FIG. 3.—Specific extinction coefficient of butadiene-styrene copolymers at various wave lengths: ◒, 262 mμ; ○, 269 mμ; ●, 265 mμ.

The fact that the absorption maximum occurs at slightly different wave lengths in polystyrene and in the copolymer introduces some uncertainty into the calculation of copolymer composition from spectrophotometric measurements. Actually the uncertainty is less than 3 per cent (relative), corresponding to the difference in E_S^* at 262 and at 260 mμ. It appears best to ignore the shift in the maximum, and to use for the calculation of x at any wave length, the value of E_S^* appropriate to that wave length. Substituting numerical values into Equation (2), we find that for measurements at 260.0 mμ:

$$x = 0.476\,E^* - 0.019 \qquad (3)$$

The accuracy of the determination of the styrene content of a copolymer by this method is considered to be about 3 per cent. The precision depends, of course, on the spectrophotometer used; for work with the Beckman spectrophotometer, the precision is better than 1 per cent. The spectrophotometric method of analysis described above can be applied only to relatively pure copolymers. Copolymers produced on a commercial scale contain appreciable

quantities of antioxidants, generally aromatic amines. These amines absorb relatively strongly in the region around 260 mμ, their specific extinction at this wave length being of the order of magnitude of 100, which is about 50 times as large as that of polystyrene. So if one has a copolymer which contains about 20 per cent styrene, and it is desired that the absorption due to the antioxidant should not cause an error of more than 1 per cent (relative) in the apparent styrene content (0.2 per cent absolute), the concentration of antioxidant in the copolymer must not exceed approximately 0.004 per cent (by weight). General plant practice is to add several per cent antioxidant to the copolymer; this means that the original antioxidant concentration must be reduced by at least 1000-fold. Experience has shown that the majority of relatively fresh copolymers can be purified to this extent, either by extraction with alcohol, or by repeated solution in benzene and reprecipitation with an excess of alcohol. It has been found, however, that polymers which have stood for a prolonged period of time (many months) cannot be readily purified to the extent required for the spectrophotometric method. It is advisable always to measure the absorption at several wave lengths to establish that the spectrum is that of the pure copolymer.

Approximate results may be obtained for samples which cannot be purified to the extent specified above by the following procedure. If one measures the specific extinction of the solution at two wave lengths, the fraction of styrene may be calculated from the difference in the extinctions at the two wave lengths on the assumption that the extinction of the impurity is the same at these two wave lengths. The assumption is approximately correct for many of the antioxidants in general use, at the two wave lengths, 260 and 275 mμ. On the basis of this assumption it may be derived that:

$$x = 0.510\ (E_{260}^* - E_{275}^*) - 0.007 \qquad (4)$$

in which E_{260}^* and E_{275}^* refer to the specific extinctions of the copolymer at 260 and 275 mμ, respectively. This approximate method should not be used if the correction for interfering absorption exceeds a few per cent.

DISCUSSION

The spectrophotometric method described in this paper may be compared with other methods for the determinination of the composition of butadiene-styrene copolymers. It has been mentioned that the only absolute method (absolute in the sense that the result is calculated from a stoichiometric relation, independent of any assumptions of a chemical or physical nature) is the determination of the carbon-hydrogen[1] ratio by precise elementary combustion analysis[4]. Among relative methods may be mentioned the iodine chloride determination of unsaturation of Kemp and Peters[4] and the determination of the refractive index of the copolymer, either in the solid form or in benzene solution[6]. The application of the former of these methods depends on the assumption that the unsaturation of the copolymer (measured by the extent of the addition of iodine chloride to double bonds) is directly proportional to the number of butadiene units present. Investigations in this laboratory have shown, however, that the method does not give the theoretical results for pure polybutadiene, and is not quite reliable for polymers of low conversion (relatively low molecular weight). In its proper sphere of application, it is estimated that the accuracy of the unsaturation method is of the order of 3 per cent.

The application of the refractive index method[6] depends on the assumption

that the refractive index of the copolymer varies in a linear manner with the composition of the copolymer, between the values for pure polybutadiene and pure polystyrene. It is clear that this assumption is equivalent to that embodied in Equation (1) of this paper; and it is found, as expected, that the refractive index method gives the same results as the ultraviolet spectrophotometric method.

Both the unsaturation method and the refraction method have the advantage, compared to the spectrophotometric method, of being equally applicable to polymers containing gel (insoluble in chloroform) and to copolymers which are completely soluble in chloroform. They have also the advantage of not being so sensitive to the presence of traces of impurities as is the spectrophotometric method, since impurities influence the results of the former methods roughly in proportion to their weight concentration.

The spectrophotometric method herein described has been applied to the determination of the composition of butadiene-styrene copolymers as a function of the degree of polymerization for various proportions of monomers. The results and their interpretation in terms of the theories of copolymer composition[7] will be reported in a subsequent paper.

SUMMARY

The ultraviolet absorption of polystyrene, with maximum absorption at 262 mμ, is due to the presence of phenyl residues in the polymer. The specific extinction coefficient is constant, *i.e.*, independent of the molecular weight of the polymer. This shows that the extinction of the phenyl residues is additive. On the basis of this fact, it is shown that the styrene content of a butadiene-styrene copolymer (such as GR-S rubber) can be determined by ultraviolet spectrophotometry. The relative precision of the determination is about 1 per cent, the probable relative accuracy is about 3 per cent.

ACKNOWLEDGMENT

This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

REFERENCES

[1] Smakula, *Angew. Chem.* **47**, 777 (1934).
[2] Hulse, Hart, French and Matheson, Private communication.
[3] Kolthoff and Dale, *J. Am. Chem. Soc.* **67**, 1672 (1945).
[4] Kemp and Peters, *Ind. Eng. Chem. Anal. Ed.* **15**, 453 (1943); Madorsky, Wagman and Rossini, private communication.
[5] A direct test of the relation between extinction and composition has been made using butadiene-chlorostyrene copolymers, in which an absolute determination of the copolymer composition can be made by determining the chlorine content. The results will be reported in a paper with H. A. Laitinen.
[6] B. L. Johnson, private communication; W. O. Baker and J. H. Heiss, private communication.
[7] Wall, *J. Am. Chem. Soc.* **63**, 1862 (1941); **66**, 2020 (1944).

THE HERTZIAN SPECTRUM OF RUBBER AND ITS MICELLAR CONSTITUTION *

PIERRE GIRARD AND PAUL ABADIE

INSTITUT DE BIOLOGIE PHYSICO-CHIMIQUE AND LABORATOIRE NATIONAL DE RADIOÉLECTRICITÉ, PARIS, FRANCE

The spectra which were studied lie within the region of hertzian frequencies, and can be represented either by dispersion curves showing the dielectric constant of the substance as a function of the frequency (or wave length λ), or by absorption curves showing the loss angle as a function of this frequency. These two types of curves represent the same phenomenon, *i.e.*, orientation of the dipolar molecules in the alternating electric field, in accordance with the theory of Debye.

The spectra and their interpretation depend chiefly on whether the molecules are crystalloid with relatively small and similar dimensions, or are colloidal, with large and unequal dimensions. In the first case, the spectra gives evidence chiefly on the form of the molecules and their structural features. Dilution in a nonpolar solvent shows for certain dipolar compounds, *e.g.*, alcohol, considerable deformations, which differ according to the solvent. In the case of colloids, *e.g.*, rubber, which has a permanent moment, the spectra and the meaning of these spectra are far different. In this case the spectra indicate that the absorption and dispersion values in the hertzian region are closely related to the micellar constitution, *i.e.*, to the different types of micelles, to their size, and to the proportion of each type.

The method used to obtain the spectra of solid rubber and solutions of rubber was to measure the dielectric constants and the loss angles (which differed according to the range of wave lengths λ) through a large band of wave lengths extending from several decimeters to thousands of kilometers.

For wave lengths from several thousand kilometers to several meters, *i.e.*, f values between 100 c.p.s. and 50 megacycles p.s., the classic bridge and resonance methods were employed. Difficulties were encountered only with the shorter wave lengths. At wave lengths lying between several meters and several decimeters, the method which was employed utilized propagation on a double line. Two parallel horizontal wires were attached at one of their extremities to a short circuit and coupled to the source of energy; at the other extremity they were connected by a smaller condenser, the dielectric of which was the substance under investigation. The length of the system constructed in this way could thus be varied. Another double line was coupled at one of its extremities perpendicular to the first double line; at its other extremity it was connected to a thermoelement connected with a galvanometer. The length of the line of measurement was varied and a curve was constructed to show the deviations of the galvanometer as a function of this length. From the maxi-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 21, No. 2, pages 39–40, February 1944. This paper represents part of a more extensive paper on the principles of a new spectral method, which has been applied by the authors on the one hand to crystalloid molecules and on the other hand to large colloidal molecules, particularly rubber, both in the solid state and in solution. The work was described by the authors at a meeting of the Société Chimique de France, November 12, 1943 (see *Compt. Rend.* 215, 84–86 (1942)).

mum position of this curve it was possible to calculate, with the aid of liquids of known dielectric constants, the true dielectric constant of the substance under investigation. From its breadth it is possible to calculate the absorption.

The results obtained by this method and by the classic resonance method at a λ value of about 4 meters agreed very well.

Figure 1 shows the absorption curve of a 20 per cent benzene solution of natural rubber depolymerized to a certain extent. The measurements were carried only to a λ value of about 1000 kilometers, but the curve is continued farther toward the right, as indicated by its broken part. The curve should tend toward zero as λ increases (taking into account the conductivity). In addition to its wide spread, the curve is characterized also by the low value of the loss angle compared with the value for crystallized molecules, whose absorption curves are bell-shaped, are much higher, and extend only a few meters. Such relatively flat and extended curves are easy to explain. They indicate the presence of numerous types of micelles, whose times of relaxation τ deviate continuously around a mean value τ_0. From the distribution equation it is

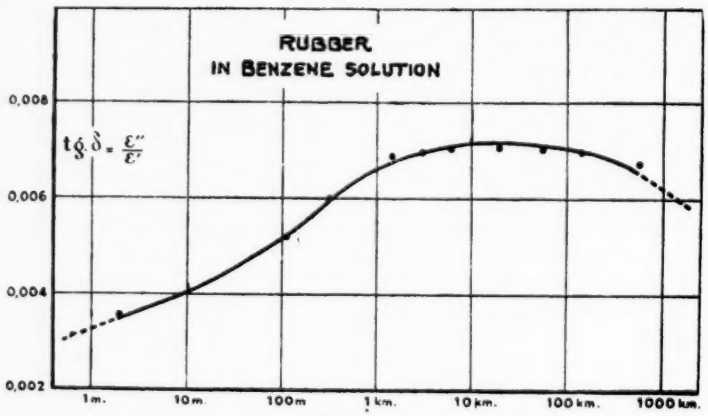


FIG. 1.

possible to derive relatively flat extended curves, with a relatively great distribution of τ values around the mean τ_0 value. These theoretical curves represent diagrammatically, according to the range through which they extend, a more or less great micellar heterogeneity. The experimental curve of any solution gives an indication, therefore, of the degree of heterogeneity, *i.e.*, of the differences in size of the micelles from the smallest to the largest.

The most interesting information is, however, that furnished by rubber in the solid state (see Figure 2). In making measurements of solid rubber, condensers of different capacities which are constructed of alternate metal plates and sheets of unvulcanized natural rubber of known composition were used[1]. A very broad adsorption range from a λ value of 50 cm. to a λ value of 5000 λ was explored, as well as a dispersion range from 300 meters to 5000 kilometers.

The characteristic which distinguishes this hertzian spectrum from that of the benzene solution is the more clearly defined limits of the absorption and dispersion regions, which makes the analysis far easier. Here we are dealing with a series of absorption curves which are well defined, are contiguous, and are of different types, and also with a series of dispersion curves, of which only

two were constructed. In the range from a λ value of 0.50 meter to a value of about 15 meters, for example, the absorption curve has the classic arched shape, quite similar to that of crystalloid molecules, and represents well defined homogeneous micelles. Beyond this range, in the range from 15 meters to 1 kilometer, the curve is broad and relatively flat, resembles the curve of the benzene solution, and represents a group of heterogeneous micelles having different times of relaxation which deviate continuously around a mean value. Between 1 kilometer and 10 kilometers and between 10 kilometers and 20 kilometers there are two dispersion and absorption curves; the first represent a homogeneous type of micelles; the second a somewhat heterogeneous type, judged by the breadth of the two curves.

Toward 3000 kilometers a new region of dispersion and of absorption apparently begins. Although the spectrum is so extensive, it is still incomplete, and it continues to the left and especially to the right toward very great wave lengths. It is intended to obtain data on the entire spectrum. The times of relaxation, or more strictly speaking, because of our present ignorance concerning the coefficient of internal friction of solid rubber, the positions of each

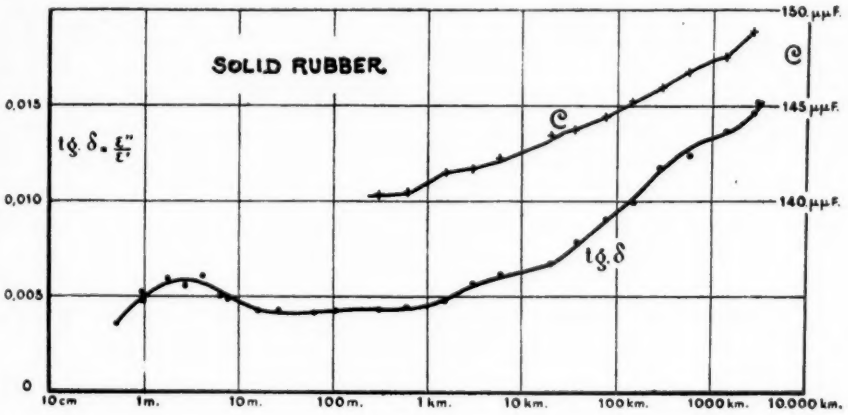


FIG. 2.

dispersion and absorption curve on the abscissa, distinguish the different types of micelles according to size; the smaller ones at the left, the larger at the right.

Finally, the height of each dispersion curve and absorption curve gives an indication of the relative concentration of each type of micelle. For example, it is evident that in the range of dispersion which begins at a λ value of about 20 kilometers, it is the micelles belonging to the fourth group which are in preponderant number.

One is led to the conclusion, therefore, that there is a fairly direct relation between the dispersion and absorption values in the hertzian range and the micellar structure, so that, with the aid of these data, it is possible to analyze fairly accurately this structure. The authors intend to follow in this way the changes in constitution of rubber in its various states, *e.g.*, when frozen, when stretched, when compressed, etc., and also to follow what happens to the micellar structure when rubber is vulcanized.

REFERENCE

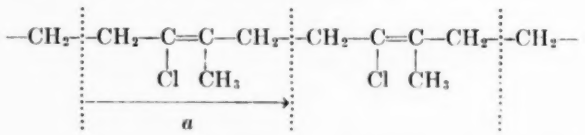
This apparatus was constructed with the help of the French Rubber Institute.

AN X-RAY STUDY OF SOME SYNTHETIC ELASTOMERS. POLYCHLOROPRENES *

HENRI FOURNIER AND JEAN JACQUES TRILLAT

Synthetic rubbers prepared from isoprene and other unsaturated hydrocarbons have been studied by means of x-rays by various investigators, including Carothers, Katz, Meyer, and Sebrell and Dinsmore. In general, these synthetic products differ markedly from natural rubber in that when they are stretched, they do not give any fibre diagrams. On the contrary, μ-polychloroprene (Neoprene), $H_2C:CCl\cdot CH:CH_2$, when stretched to about 500 per cent, gives a somewhat diffused fibre diagram with an identity period of 4.8 Å.U., corresponding to the length of a chloroprene unit in the *trans* form. We have verified this fact, and have found, in addition, that preliminary heating of the polychloroprene facilitates this orientation process which takes place upon stretching.

The investigation was continued by a study of a product which had not previously been studied, *viz.*, chloroisoprene:



Chloroisoprene likewise shows elastic properties, and is capable of being vulcanized if metallic oxides are present, *e.g.*, magnesium oxide, zinc oxide, cadmium oxide, mercuric oxide, etc. The purpose of the present work was to throw some light, first, on the molecular structure of this substance and secondly, on the mechanism of vulcanization.

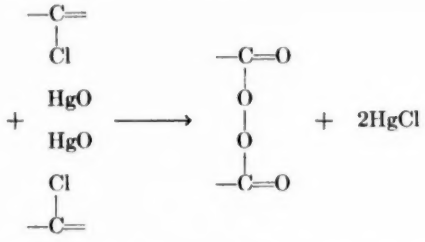
When in the pure state, and not stretched, chloroisoprene is amorphous and shows three halos; when stretched, it gives a fibre diagram which is different from that of polychloroprene. The identity period along the fibre axis, a, is 4.4 Å.U., corresponding to one chloroisoprene group. When heated beforehand up to 140° C, chloroisoprene samples show, when stretched, this phenomenon of orientation and alignment of the chains. It may be assumed, then, that the effect of heating is to modify the structure (perhaps by depolymerization and loss of chlorine) in such a way that the bonds become more ordered and consequently there is a better alignment during stretching.

Chloroisoprene does not show any notable elastic properties until a metallic oxide has been added and the mixture has been heated. This treatment corresponds to what might be called vulcanization. In a general way, the presence of compounding ingredients decreases the orientation effect brought about by stretching a heated mixture, and this seems to indicate, as in the case of rubber-sulfur mixtures, the formation of lateral bonds or bridges. It is still, however, not possible to explain satisfactorily the mechanism of this vulcanization.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 219, No. 18, pages 447–448, November 6, 1944.

In effect, certain oxides, such as mercuric oxide, cadmium oxide, lead oxide (PbO) and perhaps zinc oxide, give, after the mixtures are heated, x-ray diagrams which, in addition to evidence of unchanged chlorinated hydrocarbon, show new rings of crystalline origin, which were not present before the mixture was heated. The presence of these rings proves the presence of crystalline compounds which are formed during the vulcanization process, and which differ according to the particular oxide. In the case of mercuric oxide, it was possible to identify with certainty the compound which was formed as mercurous chloride, and not, as might have been expected, mercuric chloride. With lead oxide and with cadmium oxide, the products could not be identified for certainty, but the liberation of oxygen which accompanied the combination of the oxides with the chlorine atoms of the chloroisoprene may have given rise to oxides which were not identified by x-ray examination, and which might have been formed equally well from the chlorine-metal bond.

In any case, the x-ray diagrams show that there is a reaction between the metallic oxide and the organic compound, and that this reaction is particularly well defined in the case of mercuric oxide, where the reaction may proceed as follows:



In this way vulcanization has the effect of joining the primary valence chains laterally through the intermediary of two oxygen atoms. In addition, these bridges are formed irregularly along the chains, and the oxygen atoms are only loosely combined; hence the liberation of oxygen observed during the heating process.

It is interesting to note that this is the first time that x-rays have made it possible to obtain any definite information on the mechanism of vulcanization of synthetic elastomers.

In the case of polychloroprene (Neoprene) the results are much less well defined; the fact, however, that the diffraction rings originating from the metallic oxides in the mixtures are much less intense after heating is sufficient evidence to confirm the chemical combination described. The combined part does not reveal itself by x-ray examination, and no new compound is apparently formed, but this negative result may be due simply to the lack of sensitivity of x-ray analysis with such small amounts of material.

THE STRUCTURE OF SOME SYNTHETIC ELASTOMERS. ETHYLENE POLYSULFIDE *

JEAN JACQUES TRILLAT AND ROBERT TERTIAN

As a result of x-ray studies of different synthetic elastomers a number of works have been published which show that, in general, these products behave somewhat differently from natural rubber. When stretched, some elastomers, *e.g.*, Buna-S and Buna-N, show no evidence at all of crystallization; others, *e.g.*, Neoprene and Vistanex, show much less well defined indications of crystallization than does natural rubber. These differences in behavior leave the field open to hypotheses regarding the origin of elasticity[1].

As is well known, the condensation product of dichloroethane and sodium polysulfide gives rise to an ethylene tetrasulfide, which polymerizes in linear chains[2], $(CH_2CH_2S_4)_n$. When mixed with suitable compounding ingredients and vulcanized, this polymer gives a substitute for rubber (Thiogomme and Thiokol), which can replace the latter in certain applications.

Katz[3] and Fuller[4] have shown that stretched Thiogomme is capable of giving crystalline interferences, and a model of the elementary cell has been proposed by these investigators. The present authors have examined pure polymerized ethylene tetrasulfide and commercial Thiogomme, both when at rest and when stretched, utilizing for this purpose the K_α radiation of copper ($\lambda = 1.54$ Å.U.) The results which were obtained may be summarized as follows.

Pure polymerized ethylene tetrasulfide.—When at rest, the structure is amorphous and is characterized by a halo corresponding to a mean intermolecular distance of 10.4 Å.U. When stretched to an elongation of 50 per cent or more, a very clear fibre diagram appears, which is sharper and more intense than that of natural rubber. This diagram, in contrast to that of natural rubber, appears at very low elongations, and continues to be visible after release of the stress. The stress necessary to stretch the polymer appears to cause a plastic deformation which becomes a permanent deformation, and the oriented structure remains stabilized.

A study of the roentgenographs obtained with a cylindrical camera made it possible to calculate with great certainty the identity period along the fibre axis. This period had a c value of 4.27 Å.U., which is in good agreement with that of 4.32 Å.U. found by Katz. This value corresponds to the length of the base group $[-(CH_2)_2-S_4-]$ along the fibre axis. The proposed elementary cell is orthorhombic, with the following dimensions:

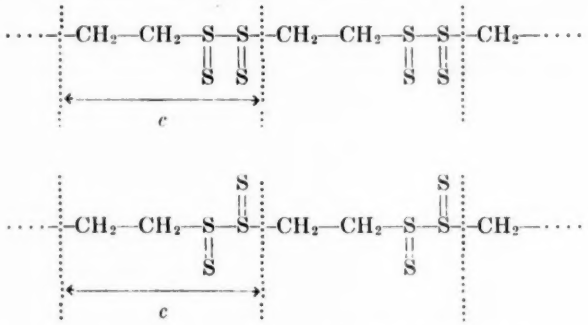
$$a = 8.57 \text{ Å.U.} \qquad b = 5.0 \text{ Å.U.} \qquad c = 4.27 \text{ Å.U.}$$

The volume would therefore be equal to 183 (Å.U.)^3, and would contain one molecule per unit cell.

The smallness of the identity period excludes the possibility of arranging the carbon and sulfur atoms along a straight line, CH_2—CH_2—S—S—S—S—

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 219, No. 16, pages 395–397, October 23, 1944.

CH_2—CH_2····, and the following structure is more probable:



This conforms to the structure proposed by Patrick[2], which was derived on a chemical basis, *e.g.*, the lability of two of the sulfur atoms.

The phenomena of crystallization brought about by stressing and manifest in polymerized ethylene tetrasulfide resemble, therefore, in many ways the crystallization of natural rubber, but differ in certain other ways, *e.g.*, in the stability of the oriented structure, which results from the high plasticity of polymerized ethylene tetrasulfide. It is probable that the mechanism involves an uncoiling brought about by the stress and the ordered arrangement of long chains previously twisted and coiled up while at rest. This uncoiling is made possible by the presence of double bonds between the sulfur atoms, and it constitutes in turn no argument in favor of these double bonds and the existence of tetravalent sulfur atoms. To our knowledge, no synthetic elastomer shows such well-defined crystallization phenomena as are brought about by these tetravalent sulfur atoms, and from this point of view alone the study of polymerized ethylene tetrasulfide is of interest.

Commercial Thiogomme.—The commercial product may contain, in addition to the polymer itself, various ingredients such as accelerators, zinc oxide, carbon black, etc. added to give it the mechanical properties desired.

The commercial product has in the unvulcanized state a particularly interesting characteristic, *viz.*, the milling effect resulting from the way in which it is manufactured imparts to it a characteristic oriented structure, quite different from that obtained by stretching.

These studies will be completed later by obtaining diagrams taken with strictly monochromatic radiation.

REFERENCES

[1] Sebrell and Dinsmore, *India Rubber World* **103**, 37 (1941); RUBBER CHEM. TECH. **16**, 857 (1943).
[2] Patrick, *Trans. Faraday Soc.* **32**, 347 (1936); RUBBER CHEM. TECH. **9**, 373 (1936).
[3] Katz, Trans. Faraday Soc. **32**, 77 (1936); RUBBER CHEM. TECH. **9**, 357 (1936).
[4] Fuller, *Chem. Reviews* **26**, 160 (1940).

THE TERMINOLOGY OF INTRINSIC VISCOSITY AND RELATED FUNCTIONS *

L. H. CRAGG

FROM THE DEPARTMENT OF CHEMISTRY, MCMASTER UNIVERSITY, HAMILTON, ONTARIO

INTRODUCTION

Although Staudinger is rightly given the credit for demonstrating the value of viscosity measurements in the study of high polymers, many workers over a period of many years have contributed ideas and techniques which together have made viscosity a function of great importance in this field. Human nature being what it is, these workers have not always been willing to use the symbols and nomenclature proposed by earlier workers; the terminological confusion that has resulted now rivals that in thermodynamics. Anyone working in this field must be aware of this confusion, but only those who have fresh memories of a survey of the literature will realize how chaotic the situation actually is.

HISTORICAL BACKGROUND

Recently, interest has more and more centered in the "intrinsic viscosity," $[\eta]$ (or, sometimes, η_i), and the viscosity functions closely related to it. The term "intrinsic viscosity" was introduced by Kraemer[1]; in 1938 he applied it[2] to the quantity $[\eta]$ defined by the expression:

$$[\eta] = \left(\frac{\ln \eta_r}{c}\right)_{c \to o}$$

where η_r = viscosity of the solution, relative to that of the solvent, and
c = concentration (grams of solute per 100 cc. of solution).

In 1935 Kraemer and Lansing[3] had used the symbol $[\eta]$ for $\lim_{c \to 0} [(\eta_r - 1)/c]$ without, however, giving it a name[4]. That the functions $(\ln \eta_r)/c$ and $(\eta_r - 1)/c$ (or, as this function is more usually written, η_{sp}/c) are in the limit $(c \to 0)$ identical had been proven several years earlier by Hess and Sakurada[5] and reaffirmed by Kraemer and Van Natta[6].

The recognition that it is desirable to use these extrapolated values in precise work has been a gradual development. The function η_{sp}/c became of interest after Staudinger had proposed his well-known rule[7] relating the "specific viscosity", $\eta_{sp}(= \eta_r - 1)$, of the high polymer solution to its concentration and to the molecular weight of the polymer: $\eta_{sp}/c = K_m \cdot M$. Objections to the rule in its original form were soon forthcoming, among them that η_{sp}/c varies with concentration and that it is the limiting value, $\lim_{c \to 0} (\eta_{sp}/c)$, that has most theoretical (and practical) significance[8]. Similarly, an empirical viscosity-concentration relationship discovered by Arrhenius[9] and used by

* Reprinted from the *Journal of Colloid Science*, Vol. 1, No. 3, pages 261–269, May 1946.

Duclaux and Wollman[10] (among others) in the form $(\log \eta_r)/c = K_c$ was applied to linear high polymers by Staudinger[7] in the form $(\log \eta_r)/c = M/K_{cm}$. This relation has been widely used, either as written or as the equivalent $(\ln \eta_r)/c = K'M$. The function $(\ln \eta_r)/c$ [or $(\log \eta_r)/c$] varies much less with concentration[11] than does η_{sp}/c, and is therefore preferred by many workers. It is not, however, independent of concentration, and in precise work an extrapolation to zero concentration is still necessary. The greater significance[12] of the limiting values of η_{sp}/c and $(\ln \eta_r)/c$ is emphasized by the fact of their identity. Since, moreover, the slope of the relative viscosity-concentration curve $d\eta_r/dc$ at zero concentration is identical with these limiting values of η_{sp}/c[6] and $(\ln \eta_r)/c$[13], the intrinsic viscosity:

$$[\eta] \equiv \lim_{c \to 0}\left(\frac{\eta_{sp}}{c}\right) \equiv \lim_{c \to 0}\left(\frac{\ln \eta_r}{c}\right) \equiv \lim_{c \to 0}\left(\frac{d\eta_r}{dc}\right)$$

would certainly seem to have a more fundamental meaning than any of the unextrapolated functions[14].

THE EXISTING CONFUSION

The importance of $[\eta]$ in molecular studies of high polymers and for the characterization of commercial high polymeric material may be taken for granted here. What we are more concerned with is the confusion that exists in the naming of $[\eta]$ and related functions. This arises from:

1. Uncertainty as to the Meaning of the Symbols

(a) η is generally accepted as the symbol for the coefficient of viscosity (the absolute viscosity) measured in centipoises. In the investigation of high polymers in solution, however, the property of interest is usually not η but η_r, the relative viscosity, *i.e.*, the ratio η/η_0 of the viscosity of the solution to that of the pure solvent. But $\eta_r = \eta/\eta_0 = \nu d/\nu_0 d_0$, where ν and ν_0 are the kinematic viscosities, d and d_0 the densities, of solution and solvent, respectively. As the kinematic viscosity is the function more directly related to the flow time of a capillary viscometer ($\nu_0 = t/t_0$ if kinetic energy corrections are negligible), it is more convenient to determine ν_r than η_r. Indeed, in many determinations of η_r the assumption is made that the solution is dilute enough to justify the neglect of the d/d_0 term[15], *i.e.*, that $d = d_0$; the quantity actually measured is therefore ν_r, the relative kinematic viscosity. When it has been proven experimentally that the density term may safely be neglected, this usage of η_r is justified; but if no such proof of the equivalence of η_r and ν_r is given, misunderstanding would be avoided if, as Wall[16] has suggested, the symbols ν_r, ν_{sp}, $[\nu]$, etc., were used in place of the less correct but more usual η_r, η_{sp}, $[\eta] \cdots$ (or, when kinetic energy corrections are appreciable but are yet not made, the symbols t_r, t_{sp}, $[t] \cdots$).

(b) In η_{sp}/c and $(\ln \eta_r)/c$, the symbol c invariably represents concentration. But that still leaves considerable scope for rugged individualism; in recent publications, c has meant the concentration expressed in the units: monomoles (Staudinger's "grundmoles") per liter of solution[17], monomoles per kg. of solution[18], grams per 100 cc. of solvent[19], grams per 100 cc. of solution[20], grams per 100 grams of solvent[21], grams per 100 grams of solution[22], grams per liter of solvent[23], grams per liter of solution[24], cc. per cc. of solution[25], cc. per 100 cc. of solution[26], cc. per liter of solution[27].

It is true that the units are usually explicitly stated, but it is also true that the statement is too often in such ambiguous terms as "volume %", "volume fractions", "grams per liter", and "base molality"[28]. It would be most helpful if workers would agree on a standard usage: fortunately a preference for the units "grams per 100 cc. of solution" (as recommended by Kraemer in his definitions of $[\eta]$[29]) is now becoming apparent.

(c) The familiar confusion involving natural and common logarithms also arises here. Notations like $\log_{10}$, $\log_e$, ln, are unambiguous, but some authors persist in the use of the unadorned "log". That this may cause serious misunderstanding is strikingly illustrated by Gee's misreading[30] of the definition of $[\eta]$ given by Busse[31], a mistake that made necessary a later correction and revision of a published paper.

2. Uncertainty as to the Meaning of the Names[32]

Again the best proof is illustration. Representative examples of names that have been applied to some of the important viscosity functions are listed in Table I.

Table I

Function	Name	Reference
η_{sp}	specific viscosity	33
	intrinsic viscosity	34
$\frac{\eta_{sp}}{c}$	reduced viscosity	35
	viscosity number	36
	intrinsic viscosity	26
	specific viscosity	37
	specific viscosity constant	23
$\lim \left(\frac{\eta_{sp}}{c}\right)$	intrinsic viscosity	38
	limiting viscosity	39
	viscosity number	40
	specific increase in relative viscosity	6
$\frac{\ln \eta_r}{c}$	specific viscosity	41
	specific viscosity constant	42
$\left(\text{or } \frac{\log \eta_r}{c}\right)$	equivalent viscosity	43
	intrinsic viscosity	44
	reduced viscosity	45
	concentration reduced solution viscosity	45
	viscosity average index	19
$\lim \left(\frac{\ln \eta_r}{c}\right)$	intrinsic viscosity	2
$\frac{d\eta_r}{dc}$	relative viscosity concentration coefficient	46
$\lim_{c \to 0}\left(\frac{d\eta_r}{dc}\right)$	relative viscosity concentration coefficient at infinite dilution	46
	or viscosity concentration coefficient	46
	coefficient of viscosity	47
	viscosity constant	48

Many of these names that are used are good, but it is not good that so many of them are used. And it is worse when the same name is used by different workers (or by the same worker at different times) with different meanings. Thus, as we have seen, *specific viscosity* is used for η_{sp}[49], for η_{sp}/c[37] and for $(\log \eta_r)/c$[50] (although, as Kraemer has pointed out, it might have been more

suitable if given to $\lim_{c \to 0} (\eta_{sp}/c)$[51]. Similarly *intrinsic viscosity*, although generally reserved for $\lim_{c \to 0} [(\ln \eta_r)/c]$ or $\lim_{c \to 0} (\eta_{sp}/c)$ or $\lim_{c \to 0} (d\eta_r/dc)$, has also been used for η_{sp}[34], for η_{sp}/c[26], and, with increasing frequency, for $(\ln \eta_r)/c$[44] especially when $\eta_r < 1.40$[52]. (There is some justification for this latter usage, for in many instances $(\ln \eta_r)/c$ is roughly constant over a relatively wide concentration range[53]; but there is not enough justification for it, for in many others $(\ln \eta_r)/c$ varies considerably with c[54], and in very few indeed is it independent.)

Now surely, if names are to be given these functions (and they will be, if only to facilitate talking about them), the names should mean the same to all workers. It is not necessary—fortunately—that each name be apt and informative; it is necessary (or at least highly desirable) that it have an unique significance[55]. As none of those who have earned the right to recommend have yet done so, the following suggestions are made in the hope that they may provoke discussion and subsequent action.

PROPOSED TERMINOLOGY

One name is suggested for each function, and one function for each name.

(a) η_{sp}

Specific viscosity

This use of the name is winning general acceptance.

(b) $\dfrac{\eta_{sp}}{c}$

Reduced viscosity

This seems to be the best of the names that have been used; it can be thought of as a shortened version of "concentration reduced specific viscosity"[45]. (The name has also been used for $(\ln \eta_r)/c$ but at a later date.)

(c) $\lim_{c \to 0} \left(\dfrac{\eta_{sp}}{c} \right)$

Intrinsic viscosity (*limiting reduced viscosity*)

The name intrinsic viscosity should be reserved strictly for this and the equivalent functions $\lim_{c \to 0} [(\ln \eta_r)/c]$ and $\lim_{c \to 0} (d\eta_r/dc)$; the temptation to use it for η_{sp}/c and especially for $(\ln \eta_r)/c$ is strong but should, on that account, be the more carefully avoided (lest one fairly good custom should corrupt the word[56]).

"Limiting reduced viscosity" follows from (b). It is not to be regarded as an alternative but rather as a supplement to intrinsic viscosity, of value in describing the method used in evaluating $[\eta]$; *e.g.*, "the intrinsic viscosity, determined as limiting reduced viscosity. . . ."

(d) $\dfrac{\ln \eta_r}{c}$

Inherent viscosity

Many names have been used for this function yet none of them seem particularly suitable: in general they are misleading or have other better established meanings. The exception, "viscosity average index", recently proposed by Tamblyn, Morey and Wagner[19], certainly has value for use as recommended, but does not suggest the close relationship between this function and $[\eta]$. The name

"inherent viscosity" is suggested because it is free of other associations and because, as a synonym of intrinsic viscosity, it serves as a reminder that $(\ln \eta_r)/c$ is (usually) very nearly but not quite the same as $\lim_{c \to 0} [(\ln \eta_r)/c]$.

(e) $\lim_{c \to 0} \left(\frac{\ln \eta_r}{c} \right)$ *Intrinsic viscosity* (*limiting inherent viscosity*)

Intrinsic viscosity is the name given this function by Kraemer and is now well established. The expression in brackets would be of value in recalling the means used to evaluate $[\eta]$, (compare (c)).

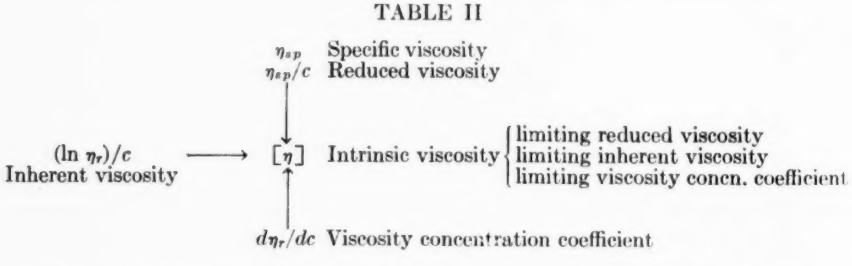
(f) $\frac{d\eta_r}{dc}$ (*Relative*) *viscosity concentration coefficient*

(g) $\lim_{c \to 0} \left(\frac{d\eta_r}{dc} \right)$ *Intrinsic viscosity* (*limiting viscosity concentration coefficient*)

The latter phrase, although cumbersome, is almost self explanatory. Its value, as a supplement to "intrinsic viscosity", is comparable to that of limiting reduced viscosity or limiting inherent viscosity.

The relationships between these functions are summarized in Table II.

TABLE II



In accordance with Wall's suggestion[16] the symbols should be written with ν in place of η where kinematic viscosities are determined and it is not clearly shown that these are numerically equal to viscosities[57]; similarly, the word kinematic should, under these circumstances, be added to each of the names. When, in addition, kinetic energy corrections are not made (and in the routine determination of these functions they usually are not) confusion would be avoided, and the purpose of the investigation would be equally well served, if use were made of the terms and symbols[16]: relative flow time t_r, specific flow time t_{sp}, reduced flow time t_{sp}/c, inherent flow time $(\ln t_r)/c$, intrinsic flow time $[t]$, etc.—unless of course it is proven that the kinetic energy correction is truly negligible.

It will be noted that, with one exception, the names recommended here are not new, but have been chosen from those already in use. An attempt has been made to choose the most satisfactory, and it is hoped that the selections may prove generally acceptable. The important thing, however, is not what choice is made but that a choice be made. A name need not be etymologically sound, but it should certainly be definitive. The first man satisfactorily performed his first task when he gave a name—any name—to each of the animals over which he had been given dominion. "And whatsoever the man called every living creature, that was the name thereof"[58].

ACKNOWLEDGMENT

The assistance given by (Miss) Hanna Hammerschlag, especially in locating examples of diversified usage, is greatly appreciated, as is the benefit derived from discussions with R. P. Graham. Grateful acknowledgment is also made of the suggestions of F. T. Wall and his permission to incorporate them in this paper.

SUMMARY

The confusion existing in the use of symbols and names for Kraemer's "intrinsic viscosity" and other functions related to it is illustrated and deplored.

The reasonable plea is made that one name be adopted for each function and that it be used with no other meaning. To stimulate discussion and ultimate action, the following names are proposed: "specific viscosity" for η_{sp}; "reduced viscosity" for η_{sp}/c; "inherent viscosity" for $(\ln \eta_r)/c$; and "intrinsic viscosity" for $[\eta]$, whether determined as "limiting reduced viscosity" $\lim_{c \to 0} (\eta_{sp}/c)$, or as "limiting inherent viscosity" $\lim_{c \to 0} [(\ln \eta_r)/c]$, or as "limiting viscosity concentration coefficient" $\lim_{c \to 0} (d\eta_r/dc)$.

Often, especially in routine practice, it is the relative kinematic viscosity ν_r that is determined; unless this is shown to be numerically equal to the relative viscosity η_r, the symbols and names of the derived functions should be modified accordingly: thus, $(\ln \nu_r)/c$ inherent kinematic viscosity, $[\nu]$ intrinsic kinematic viscosity. Frequently, also, kinetic energy corrections are neglected; under these circumstances the suggested usage is t_r relative flow time, t_{sp}/c reduced flow time, $[t]$ intrinsic flow time, etc.

Editorial Note: The Journal and author will welcome comments on this paper and on the general problem of standardizing terms and notations in the field of colloid chemistry wherever confusion exists.

REFERENCES

[1] So far as I have been able to discover, the term first appeared in print in a paper by Kauppi and Bass (*Ind. Eng. Chem.* **29**, 800 (1937)), where it was applied to a function that may readily be shown to be identical in value with Kraemer's. Nevertheless, Bass in a private communication (March 1946) states that the name "intrinsic viscosity" originated with Kraemer.

[2] Kraemer, *Ind. Eng. Chem.* **30**, 1200 (1938).

[3] Kraemer, and Lansing, *J. Phys. Chem.* **39**, 153 (1935).

[4] It has frequently been stated ("Cellulose and Cellulose Derivatives", Edited by Ott, Interscience Publishers, Inc., New York, 1943) or implied (Flory, *J. Am. Chem. Soc.* **65**, 372 (1943)) that in this paper Kraemer proposed the name intrinsic viscosity for $[\eta]$. He did recognize the need for a name for this function (see Kraemer and Lansing, *J. Phys. Chem.* **39**, 157 footnote (1935)), but did not attempt to fill it. Nor did he introduce it in the paper published by Lansing (Lansing and Kraemer, *J. Am. Chem. Soc.* **57**, 1369 (1935); see also Gee, *Ann. Repts. Progress Chem.* **39**, 7 (1942)) or in the paper published with Van Natta (Kraemer and Van Natta, *J. Phys. Chem.* **36**, 3175 (1932); see also Mead and Fuoss, *J. Am. Chem. Soc.* **64**, 277 (1942).

[5] Hess and Sakurada, *Ber.* **64**, 1183 (1932).

[6] Kraemer and Van Natta, *J. Phys. Chem.* **36**, 3175 (1932).

[7] Staudinger, "Die Hochmolekularen Organischen Verbindungen", Julius Springer, Berlin, **1932** (lithoprinted by Edwards Bros., Ann Arbor, **1943**).

[8] The limiting value of η_{sp}/c is also symbolized variously as $(\eta_{sp}/c)_{c \to 0}$, $(\eta_{sp}/c)_{c=0}$, $(\eta_{sp}/c)_0$, and η_{sp}/c_0. In this paper all these will be written $\lim_{c \to 0} (\eta_{sp}/c)$.

[9] Arrhenius, *Z. physik. Chem.* **1**, 285 (1887).

[10] Duclaux and Wollman, *Compt. rend.* **152**, 1580 (1911); *Bull. soc. chim.* [4] **27**, 414 (1920); Kraemer and Lansing, *J. Phys. Chem.* **39**, 153 (1935).

[11] Kemp and Peters, *J. Phys. Chem.* **43**, 1063 (1939); Flory and Stickney, *J. Am. Chem. Soc.* **62**, 3032 (1940).

[12] Huggins, *Ind. Eng. Chem.* **35**, 980 (1943).

[13] Flory and Stickney, *J. Am. Chem. Soc.* **62**, 3032 (1940); Matthes, *Angew. Chem.* **54**, 517 (1941).

[14] The intrinsic viscosity of a high polymeric substance is, however, not so fundamental as to be independent of the solvent, of temperature, and of the rate of shear (see, for example, the discussion in *Trans. Faraday Soc.* **40**, 274 (1944). These and other conditions of measurement should, therefore, always be described.

[15] Thomas, Zimmer, Turner, Rosen and Frolich, *Ind. Eng. Chem.* **32**, 299 (1940); Bartovics and Mark, *J. Am. Chem. Soc.* **65**, 1901 (1943); Kemp and Peters, *Ind. Eng. Chem.* **35**, 1108 (1943).

[16] F. T. Wall, private communications from Univ. of Illinois, June 1944 and July 1945.
[17] Mead and Fuoss, *J. Am. Chem. Soc.* **64**, 277 (1941); Huggins, *J. Am. Chem. Soc.* **64**, 2716 (1941); Kemp and Peters, *Ind. Eng. Chem.* **35**, 1108 (1943).
[18] Fuoss, *J. Am. Chem. Soc.* **63**, 2401 (1941).
[19] Tamblyn, Morey and Wagner, *Ind. Eng. Chem.* **37**, 373 (1945).
[20] Kraemer, *Ind. Eng. Chem.* **30**, 1200 (1938); Flory, *J. Am. Chem. Soc.* **65**, 372 (1943); Matthes, *J. prakt. Chem.* **162**, 245 (1943); Lovell, *Ind. Eng. Chem. Anal. Ed.* **16**, 683 (1944); Lyons, *J. Chem. Phys.* **13**, 43 (1945).
[21] Conrad, *Ind. Eng. Chem. Anal. Ed.* **13**, 526 (1941).
[22] Martin, cited by Pfeiffer and Osborn, in Ott, "Cellulose and Cellulose Derivatives", Interscience Publishers, Inc., New York, **1943**, p. 967; Owens, Lotzkar, Merrill and Paterson, *J. Am. Chem. Soc.* **66**, 1178 (1944).
[23] Evans and Young, *Ind. Eng. Chem.* **34**, 461 (1942).
[24] Lovell and Hibbert, *J. Am. Chem. Soc.* **62**, 2140 (1940).
[25] Bartovics and Mark, *J. Am. Chem. Soc.* **65**, 1901 (1943).
[26] Mark, "Physical Chemistry of High Polymeric Systems", Interscience Publishers, Inc., New York, **1940**, p. 280.
[27] Alfrey, Bartovics and Mark, *J. Am. Chem. Soc.* **65**, 2319 (1943).
[28] In a recent paper (Young and Harney, *Ind. Eng. Chem.* **37**, 675 (1945), for example, an otherwise unusually careful and precise definition.

$$\text{intrinsic viscosity} = \frac{\log_e \left(\dfrac{\text{viscosity of soln.}}{\text{viscosity of solvent}} \right)}{\text{concn. of polymer (g. per 100 cc.)}}$$

is marred by the omission of the noun after grams per 100 cc.
[29] Kraemer and Lansing, *J. Phys. Chem.* **39**, 153 (1935); Kraemer, *Ind. Eng. Chem.* **30**, 1200 (1938).
[30] Gee, *Trans. Faraday Soc.* **38**, 108 (1942).
[31] Busse, in "Chemistry and Technology of Rubber", edited by Davis and Blake, Reinhold Publishing Corp., New York, **1937**, p. 232.
[32] "The question is", said Alice, "whether you can make words mean so many different things".
[33] Staudinger, "Die Hochmolekularen Organischen Verbindungen", Julius Springer, Berlin, **1932** (lithoprinted by Edwards Bros, Ann Arbor, **1943**); Lyons, *J. Chem. Phys.* **13**, 43 (1945).
[34] Simha, *J. Applied Phys.* (U.S.S.R.) **13**, 147 (1942); see, however, *J. Chem. Phys.* **13**, 188 (1945).
[35] Kratky and Saito, *Cellulosechem.* **16**, 85 (1935); Meyer, "Natural and Synthetic High Polymers", Interscience Publishers, Inc., New York, **1942**, p. 23.
[36] Schulz and Blaschke, *J. prakt. Chem.* **158**, 130 (1941).
[37] Kern and Fernow, *J. prakt. Chem.* **160**, 296 (1942); RUBBER CHEM. TECH. **18**, 267 (1945).
[38] Gee, *Trans. Faraday Soc.* **40**, 261 (1944); Lyons, *J. Chem. Phys.* **13**, 43 (1945).
[39] Meyer, "Natural and Synthetic High Polymers", Interscience Publishers, Inc., New York, **1942**, p. 23.
[40] Staudinger and Jorder, *J. prakt. Chem.* **160**, 166 (1942).
[41] Duclaux and Wollman, *Compt. rend.* **152**, 1580 (1911); *Bull. soc. chim.* [4] **27**, 414 (1920); Dobry and Duclaux, *Compt. rend.* **197**, 1318 (1933); Kraemer and Lansing, *J. Phys. Chem.* **39**, 153 (1935).
[42] Berl and Büttler, *Z. ges. Schiess. Sprengstoffw.* **5**, 82 (1910); Kraemer and Lansing, *J. Phys. Chem.* **39**, 153 (1935); Staudinger, "Die Hochmolekularen Organishen Verbindungen", Julius Springer, Berlin, **1932** (lithoprinted by Edwards Bros. Ann Arbor, **1943**).
[43] Mead and Fuoss, *J. Am. Chem. Soc.* **64**, 277 (1942).
[44] Gee, *Trans. Faraday Soc.* **36**, 1162 (1940); Young and Harney, *Ind. Eng. Chem.* **37**, 675 (1945).
[45] Baker, Fuller and Heiss, *J. Am. Chem. Soc.* **63**, 3316 (1941).
[46] Flory and Stickney, *J. Am. Chem. Soc.* **62**, 3032 (1940).
[47] Goujon, *Chimie & industrie*, Suppl. to No. 8, 229 (1939).
[48] Philippoff, *Kolloid-Z.* **98**, 90 (1942).
[49] Lyons, *J. Chem. Phys.* **13**, 43 (1945).
[50] Duclaux and Wollman, *Bull. soc. chim.* [4] **27**, 414 (1920).
[51] According to Staudinger (see Reference 7), η_{sp} is the "increase in viscosity which a dissolved substance produces in a solvent"; in other words it is the specific contribution to the relative viscosity that the solute makes. In that sense, then, it is a specific viscosity. But η_{sp} varies with concentration; if "specific viscosity" is to have a meaning analogous to that of specific gravity, specific volume, specific conductance (see Reference 3), etc., it should be an intensive property of the solute. Dividing η_{sp} by c should theoretically give a function of this type, but unfortunately η_{sp}/c itself varies with concentration. On the assumption that "ideal" conditions obtain at infinite dilution, the "true" specific viscosity would be $\lim_{c \to 0} (\eta_{sp}/c)$. It may be for this reason that Kraemer regretted that the name specific viscosity had been preempted; be that as it may, it is probably just as well that another name had to be found, for, as it turned out, $[\eta]$ is not independent of the solvent used (see Gee, *Ann. Repts. Progress Chem.* **39**, 7 (1942); Kemp and Peters, *Ind. Eng. Chem.* **34**, 1097, 1192 (1942)), and a multivalued property could scarcely be considered a truly specific property.
[52] "When I make a word do a lot of work like that", said Humpty Dumpty, "I always pay it extra".
[53] Kemp and Peters, *Ind. Eng. Chem.* **33**, 1263 (1941); Flory, *J. Am. Chem. Soc.* **65**, 372 (1943).
[54] Lovell and Hibbert, *J. Am. Chem. Soc.* **62**, 2140 (1940); Baker, Fuller and Heiss, *J. Am. Chem. Soc.* **63**, 3316 (1941); Mead and Fuoss, *J. Am. Chem. Soc.* **64**, 277 (1942).
[55] In another connection, Mueller (*Am. Inst. Physics*, "Temperature, Its Measurement and Control in Science and Industry", Reinhold Publishing Corp., New York, **1941**, p. 162) has made the sage remark that "good usage is essentially a compilation of the mistakes habitually made by the right people".
[56] With apologies to Tennyson.
[57] The difference between intrinsic kinematic viscosity $[\nu]$ and intrinsic viscosity $[\eta]$, though real (see Reference 16) is very slight, and may generally be neglected.
[58] Not "those were the names thereof". My attention has been drawn to a paper by Fromm (*Kolloid-Z.* **102**, 86 (1943)), in which some carefully considered recommendations for the standardization of German usage in this field are made. Because of the difference in language, many of his proposals will not be directly helpful to English-speaking workers. It is, however, the primary purpose of the present paper to encourage just such careful consideration of our problems of nomenclature and, should a committee be formed to standardize the nomenclature, it would do well to give careful attention to Fromm's proposals.

THE THEORY OF PERMANENT SET AT ELEVATED TEMPERATURES IN NATURAL AND SYNTHETIC RUBBER VULCANIZATES *

R. D. ANDREWS AND A. V. TOBOLSKY

FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY

AND

E. E. HANSON

RESEARCH LABORATORY, THE FIRESTONE TIRE AND RUBBER COMPANY, AKRON, OHIO

Certain materials, including natural and synthetic rubbers, after being deformed for finite periods of time and then released, do not return completely to their original dimensions. This phenomenon is called "permanent set".

There are many different types of measurements, made under a great variety of conditions, all of which are described as measurements of permanent set. The molecular causes of permanent set are not the same under all of these conditions. For this reason we shall restrict ourselves in the present article to a discussion of the permanent set taking place in thin rubber samples which are maintained at constant extension at elevated temperatures. We shall show that the permanent set which occurs under these conditions is due to chemical changes which affect the structure of the rubber network, and that a quantitative molecular description of permanent set can be accomplished by the use of concepts already developed concerning the nature of these deteriorative chemical processes.

MOLECULAR SCISSION AND CROSS-LINKING: THEIR MEASUREMENT AND RELATION TO PERMANENT SET

The changes in physical properties that occur in hydrocarbon rubbers at elevated temperatures are due to the simultaneous existence of chain scission and cross-linking reactions induced by oxygen[1]. Depending on whether chain scission or cross-linking is faster in each individual case, various rubber types soften or harden as a result of exposure to air at elevated temperatures. Butyl vulcanizates tend to soften; butadiene-styrene rubbers (GR-S, for example), butadiene-acrylonitrile rubbers, and Neoprene tend to harden; natural rubber (Hevea) tends first to soften, then to harden. Intermittent measurements of the modulus of a sample maintained in a relaxed state during exposure to the elevated temperature ("intermittent relaxation") provide a method of measuring the net rate of scission and cross-linking.

On the other hand it is possible to isolate the scission reaction by measuring the decay of stress in a sample maintained at constant extension at the elevated temperature ("continuous relaxation"). The decay of stress is a direct measure of the cutting of the molecular chains of the network. The cross-linking of chains, which is occurring simultaneously, tends to take place, to

* Reprinted from the *Journal of Applied Physics*, Vol. 17, No. 5, pages 352–361, May 1946.

a first approximation, in such a way that it causes no increase of stress at constant extension. In other words, new network chains are being formed by a process of oxido-vulcanization which are in equilibrium when the sample is at the stretched length (by network chains we refer to the portions of chain molecules between contiguous network junctures).

The qualification that the cross-linking has no effect on the continuous relaxation curve "to a first approximation" is added because of the fact that, in continuous relaxation experiments carried out for extended times, an increase in stress is observed for some rubbers notably GR-S, Butaprene-N, and Neoprene, following the initial almost complete decay of stress. This increase in stress is reproducible with the same accuracy as the earlier part of the curve in which the stress decreases. A contraction of length has been observed to accompany embrittlement in unstretched thin strips resulting from heat aging.

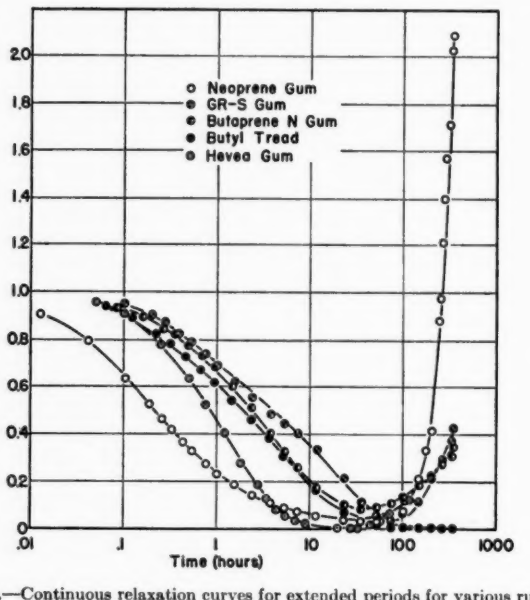


FIG. 1.—Continuous relaxation curves for extended periods for various rubber types; 130°C; 50 per cent elongation.

General theoretical considerations suggest that a contraction in volume is probably taking place. Such a contraction in volume would appear to be the most reasonable explanation of the observed increase in stress, although this has not yet been investigated experimentally. It is apparent from the Neoprene-gum curve in Figure 1 that the increase in stress may eventually become appreciable. In the case of Hevea gum the stress first decays completely to zero and later begins to increase as embrittlement of the stock sets in, following the initial softening. In Butyl stocks, which soften progressively, the stress decays completely to zero and no increase in stress whatever is observed in the continuous relaxation curves even when they are carried out to very extended times. In the continuous relaxation curves of Hevea and Butyl stocks which appear later in this paper, no error should arise from this source, since in the time intervals to which the Hevea curves were carried out, the stock was still

softening, and since the effect is not found at all in Butyl stocks. In the case of the GR-S tread stock, the relaxation curve was not carried out to times where this effect becomes significant. Nevertheless, it is well to mention this effect in any general statement concerning the nature of continuous relaxation curves.

Let us now consider the molecular changes taking place in a rubber sample which is being held at constant elongation at an elevated temperature in terms of their relation to the phenomenon of permanent set. Immediately after extension the individual molecular chains are all stretched and the equilibrium condition for all chains corresponds to the unstretched length of the sample. As the rubber remains at its constant elongation, cutting of the original chains takes place and the stress relaxes; new chains are formed by cross-linking which are at equilibrium when the rubber sample is at that particular elongation, and some of these newly formed chains are cut also. Thus at the beginning, the network chains in the rubber sample were all at equilibrium at the unstretched length; if the stress (due to chains being held out of equilibrium) eventually decays completely to zero, all the chains in the network are at equilibrium at the stretched length. At any intermediate stage between these two extremes, however, the molecular network in the rubber sample is a dual or "hybrid" network, containing chains of two types: (1) chains which are at equilibrium when the sample is at its unstretched length, and (2) chains which are at equilibrium when the sample is at its stretched length. When the external constraint holding the sample at constant extension is removed, the chains of the first type tend to pull the sample back to its original unstretched length, whereas the chains of the second type tend to hold the sample out at its stretched length. As a result, the length which the sample actually assumes is intermediate between its unstretched and stretched lengths, and its value is the length at which the stresses on each of the two sets of chains exactly balance each other.

DERIVATION OF PERMANENT SET EQUATION

Having formulated the theory of permanent set in the above qualitative way, it remains only to put the theory into mathematical form. This is done in the following way: For the case of a "homogeneous" network, in which all the network chains are at equilibrium at the same sample length, the equation relating stress and elongation in terms of the concentration of network chains in the rubber is given as follows:

$$f = skT \left\{ \left(\frac{l}{l_u} \right)^2 - \frac{l_u}{l} \right\} \tag{1}$$

where f is stress per unit attained cross-sectional area, s is the number of network chains per cc. of rubber, k is Boltzmann's constant, T is absolute temperature, and l and l_u are the attained length and unstretched length (the sample length at which the chains are at equilibrium) of the rubber sample, respectively. This equation is derived from the kinetic theory of rubber elasticity and is equally applicable both to extension and compression, *i.e.*, l may be either greater or less than l_u. A positive value of f indicates a stretching force, and a negative value a compressing force. This equation should apply to both types of chains in the rubber network. Since the equation is derived from the statistics of a single chain, it is not necessary for either type of chain to form a continuous network within the rubber sample; it is thus perfectly applicable

when one type of chain is predominant in the rubber network, chains of the other type occurring only here and there, in a relatively isolated way.

Let us denote the unstretched and extended lengths of the rubber sample by l_u and l_x, respectively, and the "set" length by l_s. We may then write for the two sets of chains in the rubber the two equations:

$$f_u = s_u kT \left\{ \left(\frac{l_s}{l_u} \right)^2 - \frac{l_u}{l_s} \right\} \tag{2}$$

$$f_x = s_x kT \left\{ \left(\frac{l_s}{l_x} \right)^2 - \frac{l_x}{l_s} \right\} \tag{3}$$

where f_u is the stress per unit attained cross-section on the chains which have their equilibrium position at the unstretched length l_u, and s_u is the number of those chains; f_x and s_x are defined correspondingly for the chains which are at equilibrium (or unstressed) at the extended length l_x. Now the condition for equilibrium in a sample with permanent set, as mentioned before, is that the retractive force exerted by the chains of type "u" is just balanced by the stretching force exerted by chains of type "x"; or, stated mathematically, that:

$$f_u = -f_x \tag{4}$$

Substituting in (4) the expressions for f_u and f_x from Equations (2) and (3), we obtain after simplification:

$$\frac{s_u}{s_x} \frac{l_x^2}{l_u^2} = \frac{l_x^3 - l_s^3}{l_s^3 - l_u^3} \tag{5}$$

Permanent set is generally expressed as the percentage of the deformation retained by the sample; stated mathematically:

$$\% \text{ Permanent Set} = \left(\frac{l_s - l_u}{l_x - l_u} \right) \times 100 \tag{6}$$

This may also be written in the form:

$$\% \text{ Permanent Set} = \frac{(l_s/l_u - 1)}{(l_x/l_u - 1)} \times 100 \tag{7}$$

which is more satisfactory for the present purpose. It is to be noted that the denominator in (7) is a constant whose value depends on the elongation at which the sample is being held in the experiment. Thus only l_s/l_u must be evaluated to calculate permanent set. We can obtain l_s/l_u from Equation (5) by algebraic transformation, giving the result:

$$\frac{l_s}{l_u} = \left[\frac{(l_x/l_u)^3 - 1}{(s_u/s_x)(l_x/l_u)^2 + 1} + 1 \right]^{\frac{1}{3}} \tag{8}$$

This expression for l_s/l_u may now be substituted in Equation (7), giving the following equation for permanent set:

$$\% \text{ Permanent Set} = \left\{ \left[\frac{C_1}{(s_u/s_x)C_2 + 1} + 1 \right]^{\frac{1}{3}} - 1 \right\} C_3 \tag{9}$$

where C_1, C_2, and C_3 are constants whose values depend on the elongation of the sample:

$$C_1 = \left(\frac{l_x}{l_u} \right)^3 - 1; \qquad C_2 = \left(\frac{l_x}{l_u} \right)^2; \qquad C_3 = \frac{100}{(l_x/l_u) - 1}$$

Thus it is to be noted that, according to this theory, the amount of permanent set in a rubber sample depends on the elongation of the sample as well as on the ratio of s_u to s_x.

To verify this relation experimentally, it is necessary to evaluate the ratio s_u/s_x in terms of continuous and intermittent relaxation curves. This can be done very simply and directly: the value of s_u/s_x at any time t is obtained by dividing the stress value given by the continuous curve at that time by the difference between the stress values of the continuous and intermittent curves. The reason for this is that the stress value given by the continuous curve is proportional to s_u, and that given by the intermittent curve is proportional to $(s_u + s_x)$, by the same factor or proportionality. There are actually no chains of type x in the intermittent sample, of course, but the number of chains of type u is equal to the sum of the number of chains of types u and x in the continuous sample. (The assumption made here, of course, is that the rates of scission and cross-linking are exactly the same in stretched and unstretched samples, so that at any given time the total number of chains is the same in both the intermittent and continuous samples.)

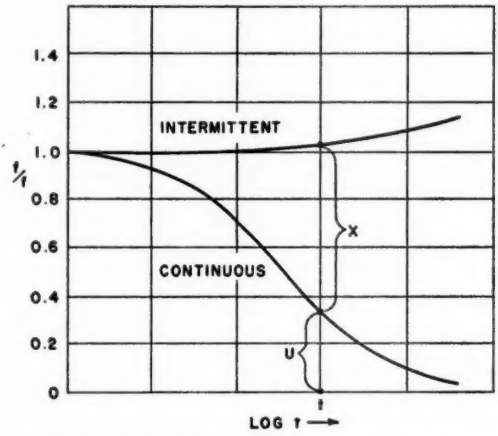


FIG. 2.—Evaluation of U and X from continuous and intermittent relaxation curves.

The stress data given in this paper are plotted as stress divided by initial stress, f/f_0, rather than absolute stress. The procedure for evaluating s_u/s_x is not affected by this fact, however. The f/f_0 value given by the continuous curve is designated as U, and the difference in the f/f_0 values of the intermittent and continuous curves as X. This is illustrated in Figure 2. Thus, according to this notation:

$$s_u/s_x = U/X \tag{10}$$

and U/X may be substituted for s_u/s_x in Equation (9), giving the following final equation for permanent set in terms of relaxation data:

$$\% \text{ Permanent Set} = \left\{ \left[\frac{C_1}{(U/X)C_2 + 1} + 1 \right]^{\frac{1}{2}} - 1 \right\} C_3 \tag{11}$$

where the constants have the same values as before. A graph of this perma-

nent set function for a number of different elongations, plotted in the form of per cent permanent set *versus* the logarithm of U/X, is shown in Figure 3.

It might be well to add a few additional remarks at this point concerning the central assumption in the theory of permanent set presented here, *i.e.*, that the cross-linking takes place in such a manner as to form chains which are relaxed when the sample is at the length at which the cross-links were formed. It is not possible to describe satisfactorily a single local cross-linking process mathematically; the effect must rather be considered as a statistical one, and it is necessary to say that the average effect of the cross-linking is to form new chains which are relaxed, just as is the case with the cross-linking taking place during vulcanization. Thus there are probably chains under a whole distribution of stress states in a sample held at constant elongation for a period of time at high temperatures. This situation is considered to be equivalent, however, to the case of a network in which there are chains of only two distinct types—chains which are at equilibrium at the original unstretched length of the sample, and chains which are at equilibrium at the stretched length. This model makes possible a mathematically simple calculation of permanent set, just as the same

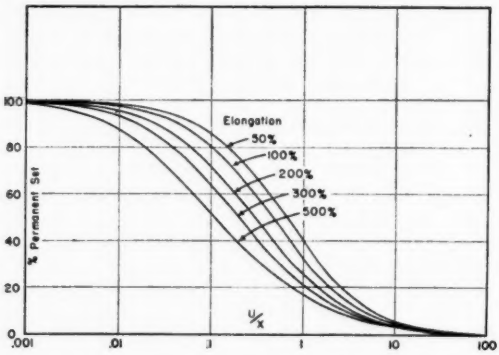


FIG. 3.—Permanent set function for various elongations.

sort of simplification makes possible the calculation of the theoretical stress-strain Equation (1), obtained from the kinetic theory of rubber elasticity. Therefore, although the picture of a "dual" network employed in the derivation above undoubtedly does not describe exactly the character of the individual chains in the network, it should describe the statistical average behavior of the individual chains.

APPARATUS AND EXPERIMENTAL PROCEDURE

The continuous and intermittent relaxation curves included in this paper were obtained in part on a beam balance type of relaxation apparatus, and in part on an inclined-plane type of relaxation apparatus. Duplicate relaxation curves from the two types of apparatus have been found to agree satisfactorily. A description of the beam balance apparatus and its operation has been given in a previous publication[2].

A sketch of the tilting apparatus is shown in Figure 4. The apparatus consists of two parts: part *A* is a brass cart for carrying as many as five 250-gram lead weights, and part *B* is a brass frame which surrounds the weight cart, but

is separate from it. The frame and the cart fit inside a glass tube along which the cart is free to roll on its four wheels. The rubber samples (*c*) used in this apparatus are flat rings ($1\frac{7}{8}$ inches outside diameter, $1\frac{1}{2}$ inches inside diameter), died from thin cured sheets (approximately 0.030 inch thick). Thin samples are used to insure complete penetration of oxygen at elevated temperatures, so that the scission and cross-linking reactions occur homogeneously throughout the samples. These samples are looped around two stainless steel pulleys, one attached to the upper end of the frame and the other to the upper end of the cart, as shown. Projecting from the lower end of the frame is a support post (*D*) with a phosphor bronze spring contact (*E*) at its upper end. The motion of the cart is arrested when a small wooden knob (*F*) fixed to the lower end of the cart touches this support post; this knob also closes the spring contact in touching the post. The support post is replaceable; posts of lengths to give the sample any elongations desired in the range of 0 to 200 per cent are easily constructed.

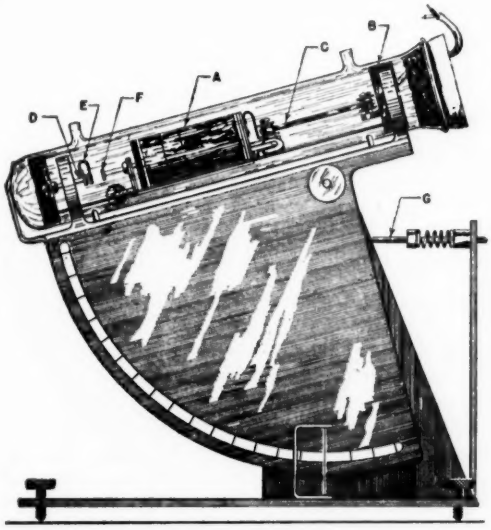


FIG. 4.—Tilting relaxometer.

The glass tube containing the apparatus is attached by clips to a tilting stand in the manner illustrated in Figure 4. The apparatus is tilted by a crank shaft (*G*) which extends through the side of the temperature box and is connected with the tilting stand through a worm gear. The entire apparatus, tube and tilting stand, is installed in an air oven with a double glass door. The temperature is thermostatically controlled to 0.3° C, and air circulation is maintained by three small air blowers. The temperature is regulated with reference to a small iron-constantan thermocouple (not shown in sketch), which is attached to the side of the sample with fine thread. The measurement of the test temperature in this way, exactly at the position of the sample, was found to be necessary to obtain the most accurate and reliable results.

In carrying out a relaxation experiment, the apparatus was first heated thoroughly at the test temperature. The tube was then removed from the oven, the sample (with thermocouple attached) looped over the pulleys, the

tube replaced in the oven with the stand at 0° tilt, the electrical leads from the spring contact connected to a neon glow bulb on the outside of the oven, and the oven closed again. When the thermocouple indicated that the sample had reached the test temperature, the sample was extended, and stress readings were begun. In taking a stress reading, the angle of tilt was slowly decreased, tapping rapidly on the crank shaft at the same time (to give the apparatus a slight vibration), until a suitable flicker was observed in the neon signal bulb (a flicker equally on and off was taken as the indication of balance). The time was noted and the angle of tilt read by means of an indicator on the base of the tilting stand; the scale on the stand is marked in half degree units, and the angle of tilt was read to 0.1 degree. In continuous relaxation experiments (in which the sample is maintained continuously at the specified elongation) the angle of tilt was maintained between readings at some value greater than that necessary to balance the stress in the sample, and was never decreased below the angle of balance, so that there was no opportunity for the sample to contract to an elongation lower than that determined by the support post. In intermittent relaxation experiments (in which the sample remains unstretched at all times, except when a stress reading is taken), the tilt was set at zero degrees between readings, the apparatus being returned to the level position immediately after each stress reading. The time required to take a stress reading on an intermittent sample was generally 15 to 30 seconds.

The weight on the sample is equal to the total weight of the cart (cart plus slotted weights) multiplied by $\sin \alpha$, the sine of the angle of tilt. When it is desired only to calculate f/f_0, the stress at time t divided by the initial stress, as a function of time (as was the case in the present work), this can be directly evaluated from the equation:

$$f/f_0 = \sin \alpha / \sin \alpha_0 \tag{12}$$

where α and α_0 are the angles of balance at times t and zero, respectively. Zero time was taken as the time of the first stress measurement for both continuous and intermittent experiments.

Measurements of permanent set were made by use of the brass frame shown in Figure 5. The frame consists simply of square bars at top and bottom held by support rods at the side, and provided with bolt clamps to hold the samples. An idea as to the size of the frame can be gained from the fact that the distance between the inside edges of the top and bottom bars is $6\frac{1}{4}$ inches. (Figure 5 is drawn to scale.) The frame will hold as many as five samples.

The samples used were small strips $\frac{1}{4}$ inch wide and approximately 6 inches long, cut from the thin vulcanized sheets from which relaxation samples are obtained. Two fine silver ink marks were placed on the edge of each sample an appropriate distance apart, and the distance between marks was measured accurately for each sample with a millimeter rule. The samples were then fastened to the frame, stretched to the desired elongation, and the distance between marks again accurately measured. The frame was inserted in an air oven, whose temperature was thermostatically controlled to $\pm 0.3°$ C, the temperature being indicated by a thermometer with its bulb adjacent to the frame. The frame was suspended from a nail on the back wall of the oven by means of a small L-bracket attached at the end of the top cross-bar of the frame, so that the frame projected sidewise perpendicularly from the oven wall. When it was desired to remove a sample at various time intervals, the frame was removed from the oven, the sample quickly cut loose with scissors,

and the frame immediately replaced in the oven. After the samples had cooled for five minutes, the distance between ink marks was again measured, and the permanent set of the sample calculated by the equation:

$$\% \text{ Permanent Set} = \frac{l_s - l_u}{l_x - l_u} \times 100 \tag{13}$$

The original distance between marks l_u, the distance when the sample was stretched on the frame l_x, and the distance after removal of the sample from the oven l_s, were each measured to an accuracy of 0.1 mm. and the permanent set was calculated to 0.1 per cent. Appropriate time corrections were applied for the time required for the oven to reach temperature after inserting the frame and for the time in which the frame was out of the oven to remove samples; the corrections necessary were small in each case.

FIG. 5.—Permanent-set frame.

In one case, *i.e.*, the permanent set measurements on GR-S tread stock at 130° C, a slightly different procedure was followed in cutting the samples from the frame. In these measurements the samples were cut loose at one end, without opening the oven, by the use of a razor blade attached to a rod which was manipulated through a small aperture in the back of the oven. One minute later the oven was opened, and the sample was cut free from the frame with scissors, without removing the frame from the oven. The permanent set was measured 5 minutes after removal of the sample from the oven, as before, and in all other respects the procedure was the same as that used for the other stocks. This modified procedure was used to avoid any cooling of the sample before cutting, which would result in the formation of "secondary" interchain bonds in the sample, which in turn would cause an error in the permanent set

value. This effect will be discussed in more detail in the section on experimental results.

The time interval of 5 minutes between removal of the sample from the oven and measurement of permanent set was chosen to allow the sample to cool completely to room temperature. The recovery observed on standing of the samples at room temperature was quite small, as can be seen from the data in Table I. Recovery was measured at intervals of one hour, one day, and

TABLE I

RECOVERY AT ROOM TEMPERATURE

Stock	Percentage permanent set after recovery times of			
	0 hr.	1 hr.	1 day (22 hr.)	1 week (169 hr.)
Hevea gum	58.3	57.9	56.6	56.0
Butyl gum	42.9	42.9	42.5	42.3
Butyl tread	57.3	57.3	56.3	55.5
GR-S tread	60.9	60.3	59.3	58.9

one week after the original permanent set measurement. Samples of the four different rubber stocks studied in this paper were used, each of which was exposed for two hours at 130° C, at 50 per cent elongation. It is seen that the recovery was less than 3 per cent in every case after a week had elapsed, and was particularly small in the case of Butyl gum.

EXPERIMENTAL RESULTS

Results of permanent set measurements, in which experimental permanent set values are compared with permanent set predicted from continuous and intermittent relaxation curves by means of the permanent set theory developed above, are shown in Figures 6–10. These experiments were planned to include

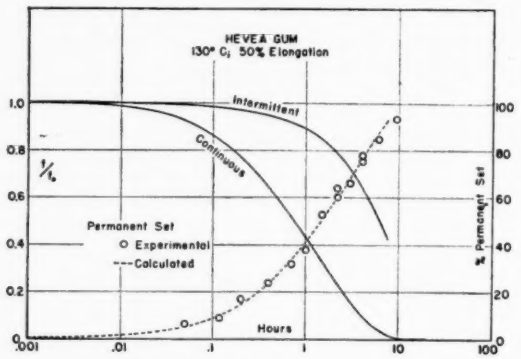


FIG. 6.—Permanent set as a function of time for Hevea gum stock at 130°C and 50 per cent elongation.

as many variables as possible: different polymer types, gum and tread type stocks, different temperatures, and different elongations. Four different rubber stocks were used in these experiments: Hevea gum, Butyl gum, Butyl tread, and GR-S tread. The compounding and cure of these stocks are given in Table II.

Permanent set results for Hevea gum stock at 130° C and 50 per cent elongation are shown in Figure 6. The continuous and intermittent relaxation curves are drawn in as solid lines; and the theoretically predicted curve of permanent set as a function of time, calculated from the relaxation curves, is drawn as a dashed line. Experimental permanent set points are shown as circles, each point, of course, being obtained from a separate sample. It is seen that the agreement between experiment and theory is excellent.

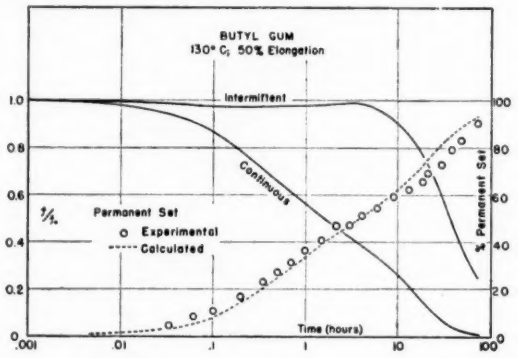


FIG. 7.—Permanent set as a function of time for Butyl gum stock at 130°C and 50 per cent elongation.

Similar data for Butyl gum and Butyl tread at 130° C and 50 per cent elongation are shown in Figures 7 and 8. Although the agreement between the experimental points and the theoretically calculated permanent set curves is not as precise here as was the case for Hevea gum, the agreement must nevertheless be regarded as satisfactory. Duplicate permanent-set points were obtained for Butyl gum at 1.00 hour; 2.20 hours, and 4.10 hours. The agreement between these duplicate samples was so close that it was impossible to draw two separate points; for this reason these points are indicated by half circles in the graph.

TABLE II

COMPOUNDING OF STOCKS

Type of stock	Hevea gum	Butyl gum	Butyl tread	GR-S tread
Polymer:				
Hevea smoked sheet	100			
GR-I		100	100	
GR-S				100
Sulfur	3	2	2	2
Zinc oxide	3	5	5	5
Stearic acid	0.5	1.5	3	3
Captax	1	0.5	0.5	1.5
Tuads		1	1	
Agerite powder	1			
Bardol				5
Channel black			50	50
Cure	75 min. at 270°F (132.2°C)	75 min. at 300°F (148.9°C)	100 min. at 300°F (148.9°C)	100 min. at 270°F (132.2°C)

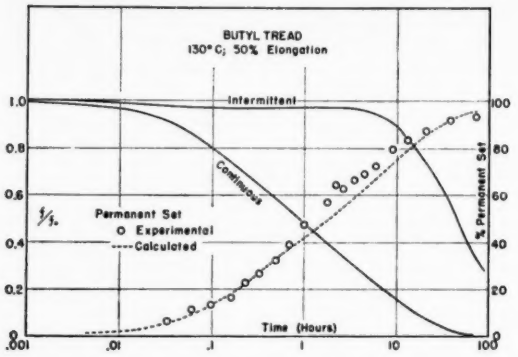


FIG. 8.—Permanent set as a function of time for Butyl tread; 130°C; 50 per cent elongation.

Relaxation and permanent set data are shown for GR-S tread at 130° C and 50 per cent elongation in Figure 9. In this stock, molecular cross-linking takes place more rapidly than scission, unlike the Hevea and Butyl stocks, in which the reverse is true. Nevertheless, it is seen that the agreement between experimental and calculated permanent set values is rather good in this case also.

It will be remembered that in this particular experiment the permanent set samples were cut at the test temperature while the oven remained closed, rather than immediately after removal of the set frame from the oven, as was the case in the other permanent set measurements reported here. This was found to be necessary because of the formation of stable "secondary bonds" in

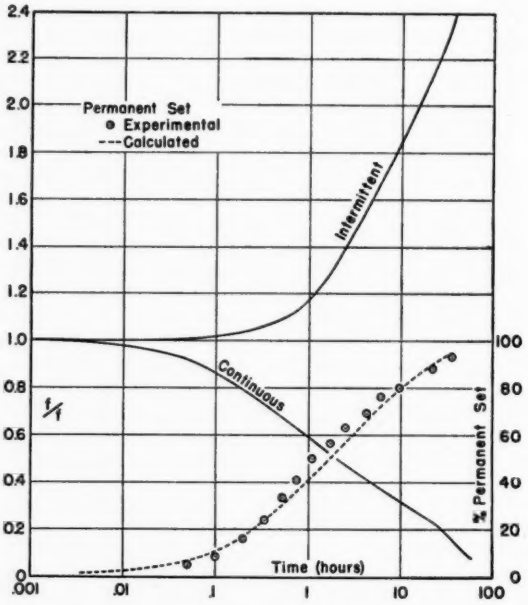


FIG. 9.—Permanent set as a function of time for GR-S tread; 130°C; 50 per cent elongation.

the sample as a result of the cooling which took place on removal of the frame from the oven, before the samples could be cut. These so-called secondary bonds are not primary chemical valence bonds, but rather are weak physical interchain bonds (possibly of a dipole-dipole or van der Waals type) which are quite unstable at very high temperatures, but whose stability increases as the temperature is lowered. Since in terms of stress phenomena (such as permanent set) a secondary bond which has not broken has the same effect as a primary valence cross-link, the formation of stable secondary bonds by cooling of a sample at its extended length is the same as if an increased amount of primary valence cross-linking had taken place; *i.e.*, the observed permanent set is increased. It is found experimentally that permanent set values obtained from GR-S tread samples cut from the frame immediately after removal from the oven are a few per cent greater than the values obtained from samples cut in the oven at test temperature; and when the frame is removed from the oven and the samples allowed to cool a few minutes before cutting, the permanent set values obtained are very markedly greater than the values obtained

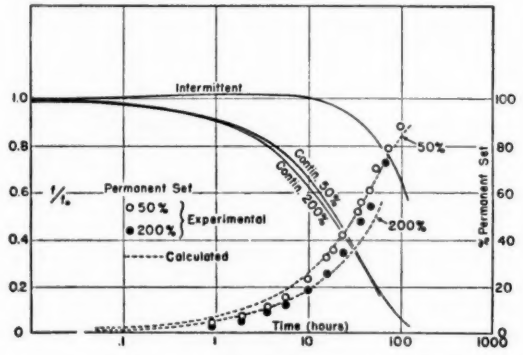


FIG. 10.—The effect of elongation on permanent set. Hevea gum at 50 and 200 per cent elongation; 100°C.

from duplicate samples exposed for the same length of time to the elevated temperature but cut at test temperature with the oven closed. GR-S tread stock shows large secondary bond effects in general. When permanent set samples of the other stocks were cut at the test temperature in the same way, the permanent set values obtained from Hevea gum and Butyl gum samples did not differ significantly from the results in Figures 6 and 7; permanent set values of Butyl tread samples were slightly less than the values in Figure 8, thus slightly improving the agreement between experiment and theory. There was apparently a slight secondary bond error in the case of Butyl tread; in general it is observed that secondary bond effects are greater in tread stocks than in the corresponding gum stocks. It would undoubtedly be best to cut permanent set samples at test temperature as a standard procedure, to avoid any error due to this source.

In Figure 10, permanent set data are shown for Hevea gum at 100° C at both 50 per cent and 200 per cent elongation. Theoretical permanent-set curves have been calculated for both elongations from the continuous relaxation curves at the two elongations and the intermittent curve (obtained at 50 per cent elongation) which are shown in the graph. The same intermittent curve

was used for both calculations, since the elongation of the intermittent sample is really 0 per cent in both cases, and intermittent curves in which the stress is measured at different elongations should give the same f/f_0 curve. It is seen that the experimental permanent-set points for 50 per cent elongation agree well with the calculated 50 per cent curve. The 200 per cent elongation experimental points agree satisfactorily with the calculated 200 per cent curve at the earlier times, but for some reason rise somewhat above the calculated curve at the later times, having values more nearly like those of the 50 per cent points than is predicted from the relaxation curves. The 200 per cent experimental points appear to give a smooth curve, just as the 50 per cent points do, so that apparently the effect is not fortuitous. The explanation for this deviation is not known. There is a definite difference between the 50 per cent and 200 per cent experimental permanent-set points, however, the 200 per cent points being lower than the 50 per cent points, which agrees with the predictions of the theory.

The generally satisfactory agreement of experimental permanent-set data with predicted permanent-set, calculated from continuous and intermittent stress relaxation curves by means of the permanent-set theory developed in this paper, appears to offer a rather good confirmation of the general correctness of the molecular picture of permanent set at elevated temperatures upon which this quantitative permanent-set theory is based.

ACKNOWLEDGMENT

This work was done at Princeton University with the coöperation of the Firestone Physics Research Group. The authors wish to thank F. S. Grover for his work in constructing the tilting relaxometer. Valuable suggestions made by H. S. Taylor and J. H. Dillon are gratefully acknowledged. The permission of the Firestone Tire and Rubber Company, who sponsored this work, to publish these results is appreciated.

RESUMÉ

A molecular theory is developed to describe quantitatively the permanent set which takes place in thin samples of vulcanized natural and synthetic rubbers held at constant extension at elevated temperatures. Permanent set is considered to be the result of the formation, through the action of molecular scission and cross-linking reactions, of a dual molecular network in the rubber sample, in which the network chains are of two types: chains which are at equilibrium when the sample is at its unstretched length, and chains which are at equilibrium when the sample is at its stretched length. According to the theory, the amount of permanent set in a rubber sample is a function of only two quantities: the relative ratio of the number of chains of the two types, and the elongation at which the sample was held. Experimental data on permanent set for various rubber types and under different conditions are presented and are shown to be in good agreement with the theory.

REFERENCES

[1] Tobolsky and Andrews, *J. Chem. Phys.* **13**, 3 (1945).
[2] Tobolsky, Prettyman and Dillon, *J. Applied Phys.* **15**, 380 (1944).

APPLICATIONS OF INFRARED METHODS IN THE STRUCTURAL EXAMINATION OF SYNTHETIC RUBBER *

J. E. Field, D. E. Woodford, and S. D. Gehman

Research Laboratories, The Goodyear Tire & Rubber Company, Akron, Ohio

INTRODUCTION

Infrared absorption spectra have been long recognized as a convenient means for studying the structure of organic molecules. The interpretations of the spectra are based on the energy interactions of the molecule and the radiations which arise from the vibration of the constituent atoms and molecular rotations. For simple or highly symmetrical molecules, the determination of the normal modes of vibration and the calculation of the absorbing frequencies are relatively simple and straightforward. For more complicated organic molecules, this becomes increasingly difficult because with each additional atom, the number of degrees of freedom is increased by three and the determination of the normal modes of vibration becomes practically impossible. However, interpretations can be made to a useful extent through empirical comparisons with the absorption spectra of simpler known structures.

The data that have been accumulated by investigators in this field have made it possible to assign rather definite absorption frequencies to some of the chemical linkages and functional groups. These correlations which have appeared in numerous places in the literature are partially reproduced in Table I.

Table I

Frequency range	Chemical linkage
3000–4000 cm^{-1}	CH, OH, NH
2000–2500 cm^{-1}	C≡C, C≡N
1350–2000 cm^{-1}	CH_3, CH_2, CH, C=C, C=O
900–1000 cm^{-1}	C=C

Organic compounds generally have strong absorption bands below 1300 cm^{-1}, to which few definite assignments can be made with certainty because the vibrations of many of the atoms of the molecule may be involved rather than a specific part of it. It is clear that such empirical relationships must be relied upon in studying the structural variations of the long chain, complex molecules which occur in butadiene and isoprene polymers and copolymers and other synthetic rubbers. This procedure has been applied to determine the effects of oxidation and of variations in monomers and polymerizing conditions on the structure of synthetic rubber. It is practically certain that physical deficiencies of synthetic rubber are due principally to the structure of the long chain molecules rather than to the chemical nature of the monomers used.

* Reprinted from the *Journal of Applied Physics*, Vol. 17, No. 5, pages 386–392, May 1946.

EXPERIMENTAL PROCEDURE

A conventional Littrow type rocksalt prism spectrometer of our own design and construction, shown in Figure 1, was used for obtaining the absorption records. The refracting faces of the 60-degree prism are 15 cm. long by 10 cm. high. The current from the vacuum thermocouple is conducted to a galvanometer, the deflections of which actuate a photocell amplifier. The absorption curves are automatically recorded by a Leeds and Northrup Speedomax, which operates from the amplifier. These curves show the absorptions (not percentage absorption) by the varying galvanometer deflection recorded as a function of the wave number setting of the Littrow mirror.

The samples were prepared in most instances by evaporating the solvent from polymer solutions poured on rocksalt plates, thus leaving a thin film of

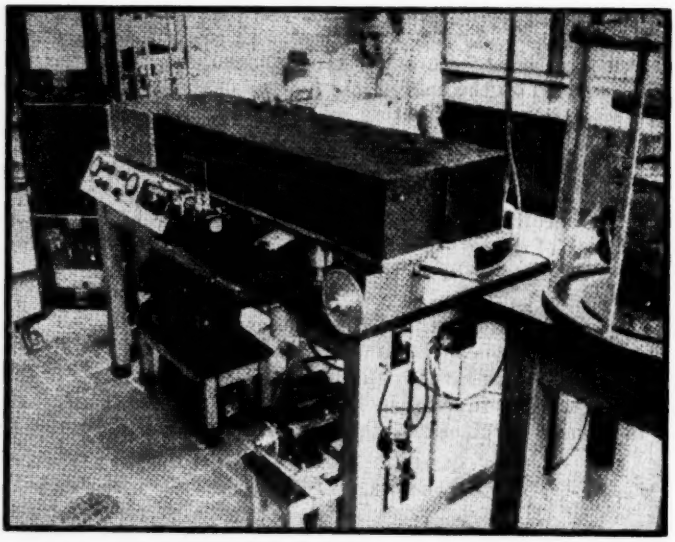


FIG. 1.—Spectrometer and recorder.

polymer for examination. The thickness of the film was adjusted for about 10 per cent transmission of the 1450 cm^{-1} band. This was rather easily accomplished by controlling the concentration of the solution and by the use of successive layers of film. The latex samples were prepared by placing a few drops in a closed glass frame floating on a mercury surface. To prevent undue oxidation, these films were first dried in an atmosphere of nitrogen, and then in a vacuum desiccator. Since the film thickness of the various samples was maintained essentially the same, a fair estimate of the intensity of the absorption of a particular band can be made relative to a corresponding one of another sample without transforming the absorption curves into terms of per cent transmission.

ABSORPTION SPECTRA OF VARIOUS POLYMER CHAIN STRUCTURES

The chemistry of polymerizing reactions is rather complex in character. Any discussion concerning the general principles and mechanisms of such

reactions need not be entered into here. However, to understand the absorption spectra of polymers of butadiene and isoprene, which have played such an important role in the development of synthetic rubber, it is necessary to point out the various ways in which polymerization of these diolefinic monomers can proceed. These are diagramatically shown in Figure 2. The struc-

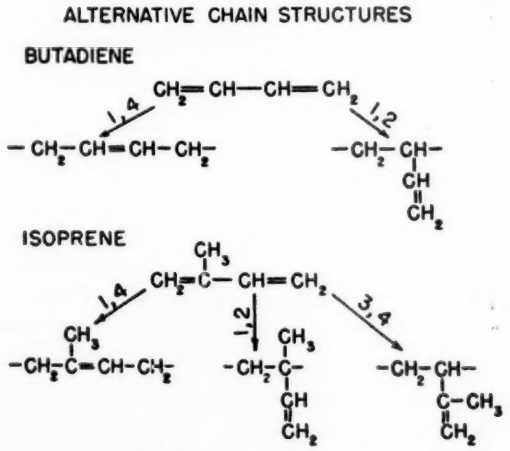


FIG. 2.—Alternative chain structures for polybutadiene and polyisoprene.

tures appearing at the double bonds may be typified in the manner shown in Table II. Compounds which can be differentiated according to the above classification are known to have characteristic absorption frequencies which will be of considerable value in the interpretation of the absorption spectra to be discussed.

TABLE II

Polybutadiene	
1,4 addition	$R_1CH{=}CHR_2$
1,2 addition	$RCH{=}CH_2$
Polyisoprene	
1,4 addition	$R_1R_2C{=}CHR_3$
1,2 addition	$RCH{=}CH_2$
3,4 addition	$R_1R_2C{=}CH_2$

POLYBUTADIENE AND GR-S

The absorption curves for sodium and emulsion polymers of butadiene are shown in Figure 3. The differences appearing in the two spectra are quite significant. That a high degree of 1,2-polymerization occurs in the sodium polymer has been previously deduced from ozonolysis and infrared work[1]. This is recognized by the appearance of the very strong band at 996 cm^{-1}, which is characteristic of compounds of the type $RCH{=}CH_2$[2]. A relatively weak band appears at this frequency for the emulsion polymer. Absorptions are present in both polymers at 967 cm^{-1}, which is characteristic of compounds of the type $R_1CH{=}CHR_2$. The bands at 914 cm^{-1} and 1450 cm^{-1} appear to be split into doublets in the sodium polymer, evidently because of the influence of the large number of terminal double bonds.

In the development of synthetic rubber of the GR-S type, it was found that emulsion polymers possessed the more desirable physical properties and process-

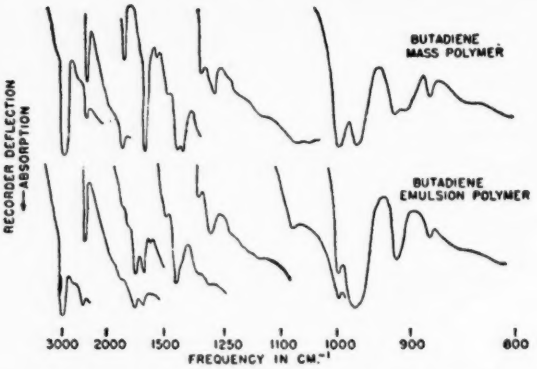


FIG. 3.—Absorption curves for sodium and emulsion polymers of butadiene.

ing qualities. Since the product of a reaction of this type for butadiene leads predominately to the 1,4-structure, it is thought that the relative amounts of these two structures in the copolymer has some bearing on these physical characteristics because butadiene is the principal constituent in the GR-S type of synthetic. Accordingly, methods have been sought to obtain quantitative determinations of relative amounts of 1,2- and 1,4-structure in polymers and the GR-S copolymer. Infrared methods afford a positive and direct way of carrying out such analyses. The following procedure has been found to be convenient for this purpose. Referring to Figure 4, which illustrates the re-

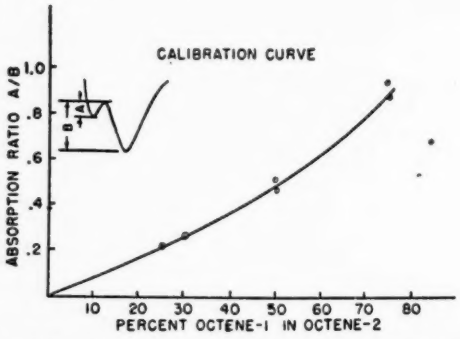


FIG. 4.—Calibration curve for determining the amount of 1,2-structure in polymers and copolymers of butadiene.

sultant band due to the two overlapping bands at 996 and 967 cm^{-1}, it is evident that the ratio A/B can be used for characterizing the band structure. If this ratio can be calibrated in terms of known relative amounts of the two structures, the infrared absorption spectrum immediately becomes applicable as a method of determination. To do this, absorption spectra were obtained for two compounds, one having a terminal double bond and the other an internal double bond. Pure samples of 1-octene and 2-octene were used for this purpose. The spectra of known mixtures of these hydrocarbons were obtained and the ratio A/B was determined from the absorption curves. This ratio

was then plotted as a function of per cent 1-octene shown in Figure 4. It is then assumed that this curve applies for the butadiene polymers and copolymers. This assumption may not be entirely valid, since other structural effects on these bands are not considered, but it seems reasonable to believe that a very close approximation can be reached with this method. Following the procedure outlined above, the results for several typical polymers are given in Table III.

TABLE III

Type of polymer	Ratio A/B	Percentage 1,2-addition
Polybutadiene (emulsion)	0.187	21
Polybutadiene (sodium)	1.1	80
GR-S (production)	0.180	19

The GR-S sample included in the above table was a typical production sample. It is of interest because it shows that the amount of 1,2-structure determined by this method is within reasonable agreement with estimates obtained by other methods. The extremely high percentage shown for the sodium polymer may not be so accurate, since the method appears to be less sensitive for mixtures with such high ratios.

POLYISOPRENE

The absorption spectra for the emulsion and sodium polymers of isoprene are shown in Figure 5. The structural study of this polymer is of particular interest because the monomer unit is the same as for natural rubber, and yet

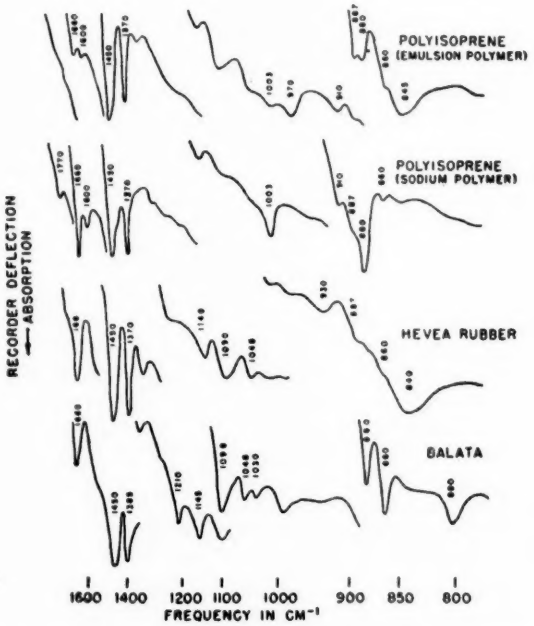


FIG. 5.—Absorption curves for comparing the structure of Hevea rubber, Balata, and the emulsion and sodium polyisoprenes.

the structure and physical properties of the latter cannot be reproduced in the synthetic product. The absorption spectra for Hevea rubber and Balata are included in this figure for the purpose of comparison.

If the isoprene is polymerized by 1,4-addition, the structure type would be $R_1R_2C{=}CHR_3$, which corresponds to the structure of Hevea rubber. Compounds of this general type have a characteristic band around 840 cm^{-1}. A band does appear here for the emulsion polymer indicating that this structure is present. In comparing this spectrum with the one for Hevea, it is observed that, although there are some striking similarities, the structures of the two are not identical. However, they do have more in common than do the sodium polymer and Hevea. On this basis, it is reasonable to believe that the emulsion product of polyisoprene is chiefly of the 1,4-structure.

If the polymerization reaction proceeds by 1,2-addition, the resulting compound would fall in the $RCH{=}CH_2$ class. This is the same general type as the 1,2-addition of butadiene, and strong bands would be expected to appear around 996 cm^{-1} and 914 cm^{-1}. Rather weak bands do appear in these regions for the emulsion polymer, while relatively stronger ones are present in the spectrum of the sodium polymer. Thus, a small amount of this structure is indicated in both of these polymers.

The absorption spectrum for the sodium polyisoprene shows a very strong absorption band at 881 cm^{-1}. Compounds having the general structure $R_1R_2C{=}CH_2$ are known to have absorption bands in this region. Accordingly, this type of compound would correspond to the 3,4-addition of the polyisoprene structure. The absence of the bands at 840 cm^{-1} and 970 cm^{-1} and the intense absorption at 881 cm^{-1} lead to the belief that the structure of this polymer is predominantly of the 3,4-type.

Balata, the absorption spectrum of which is included in Figure 5, is generally presumed to be a *trans*-isomer of Hevea rubber. This *cis-trans*-isomerism causes distinctive differences in the infrared absorption spectra[3]. Comparison of the spectra for these natural products with those for synthetic polyisoprenes does not disclose the presence of any appreciable amount of the *trans*-isomer in the synthetic polymers. This is particularly interesting because there has been speculation that the inferiority of the synthetic polymers to Hevea rubber might arise from the fact that a mixture of *cis*- and *trans*-structure occurs in the synthetic polymers.

EFFECTS OF OXIDATION

The effects of exposure of GR-S films to air under conditions such as to accelerate oxidation are shown in the absorption curves appearing in Figure 6 and Figure 7. The samples were all prepared from a master solution of production GR-S in benzene, from part of which the antioxidant (phenyl-β-naphthylamine) was removed by reprecipitation. Films with and without antioxidant were exposed to ultraviolet light (Atlas Fadeometer, violet arc) for at least twenty-four hours at a constant temperature of 40° C. Similar films were heated for twenty hours in air at 103° C. The absorption curves resulting for films without antioxidant are shown in Figure 6. The control or untreated sample is represented in the top curve. The structural changes initiated by exposure to ultraviolet light are evident in the middle curve. New bands appear at approximately 3500 cm^{-1} and 1720 cm^{-1}, which are definitely due to O—H and C=O linkages, respectively. These groups have been identified chemically in oxidized natural rubber[4]. Increased absorption is also

noted in the 1050 cm^{-1} range. The relative intensities of the 996 and 967 cm^{-1} are difficult to interpret. The absorption in the vicinity of the 996 cm^{-1} band is increased, but the significance of this is confused by the generally increased absorption over this whole region. The decrease in the intensity of the 914 cm^{-1} band probably is indicative of a definite decrease in the total number of double bonds, which would be expected with oxidation reactions.

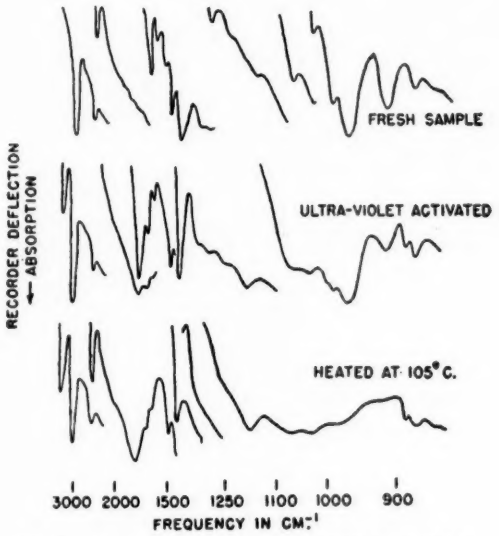


FIG. 6.—Absorption curves showing oxidation of GR-S in the absence of antioxidant.

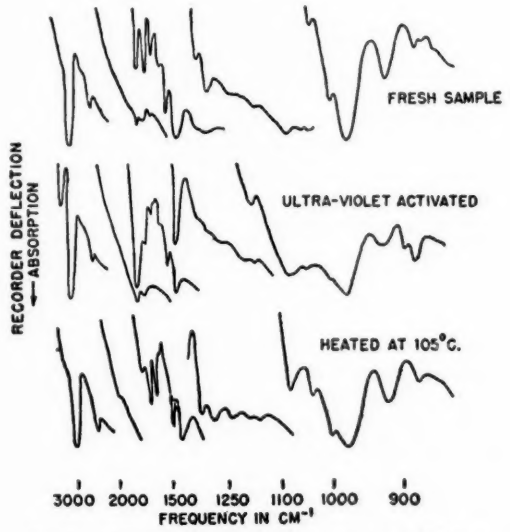


FIG. 7.—Absorption curves showing oxidation of GR-S in the presence of antioxidant.

When a similar sample was heated for twenty hours in air at 105° C, a number of differences appear in the absorption record when compared with that for the ultraviolet activated sample. This is represented in the bottom curve of Figure 6. The intensity of the O—H band has increased noticeably. The carbonyl band at 1720 cm^{-1} has broadened considerably. Since the absorptions for the various carbonyls occur at slightly different frequencies, it is possible that the broadening of this band might be due to additional types of carbonyls. The absence of the 914 cm^{-1} band indicates a rather complete saturation of the double bonds. There is a general region of heavy absorption extending from about 900 cm^{-1} to 1300 cm^{-1}, probably indicating heterogeneity in the structure brought about by oxidation. The structure responsible for the occurrence of the 890 cm^{-1} band on oxidation is not definitely known, but its position suggests the type $R_1R_2C{=}CH_2$.

In examining the absorption curves of Figure 7 corresponding to samples with antioxidant, it appears that ultraviolet activation is the only agency that has produced any appreciable structural changes. These changes are similar to the ones which occurred for the sample without antioxidant. With the

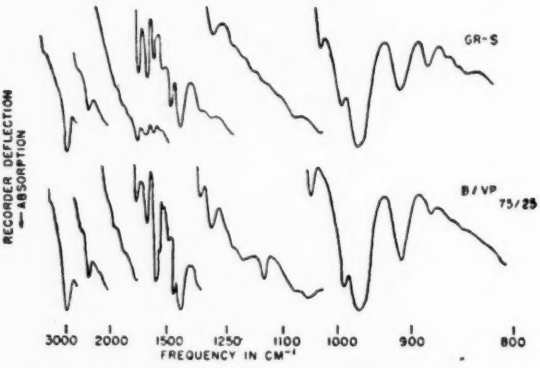


FIG. 8.—Absorption curves comparing the structure of GR-S and a copolymer of butadiene and vinylpyridine.

antioxidant present, twenty hours exposure in air at 105° C produced no noticeable structural changes. It is very interesting that structural changes due to heat treatment were inhibited by the antioxidant, whereas this antioxidant had little influence on the effects caused by ultraviolet activation. Apparently, the mechanisms of oxidation are different in the two cases.

MISCELLANEOUS POLYMER STRUCTURES

An absorption curve for a typical butadienevinyl pyridine copolymer is reproduced in Figure 8, together with one of the GR-S for comparison. Although many of the bands are very similar in character, there are several differences that can be observed. One is the relative increase in the intensity of the 1590 cm^{-1} band in the vinyl pyridine copolymer. This band is usually attributed to aromatic double bonded carbons, but the presence of the nitrogen in the aromatic group becomes evident with an additional absorption at 1570 cm^{-1}. There is a shift toward the longer wave-lengths of the aromatic CH bending frequencies around 1490 cm^{-1} and a characteristic band at 1150 cm^{-1}.

Hence these two synthetic rubbers can be readily distinguished by their infra-red spectra. It is noteworthy that the overlapping bands at 996 cm^{-1} and 967 cm^{-1} are so very similar for the two types of rubber.

Absorption curves are shown in Figure 9 for samples of GR-S in which different mercaptan type modifiers were used in the polymerization. These films also contained phenyl-β-naphthylamine as antioxidant. Since the presence of modifiers during polymerization influences the physical properties of

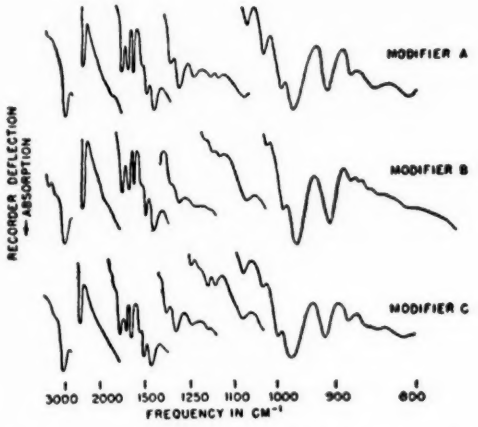


FIG. 9.—Absorption curves showing the effect of modifiers on the structure of GR-S.

the product, it was thought that structural differences might be detected in these absorption spectra However, the absorption curves for polymers made with these three modifiers are strikingly similar. Since the 996 cm^{-1} band shows no evident difference in the number of side vinyl groups present and other differences in the spectra are insignificant, it can be concluded that these three modifiers influence the structure in much the same way, at least as far as can be detected by infra-red methods. In this case, there appears to be

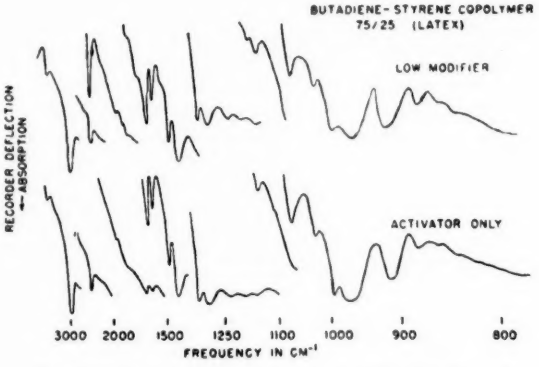


FIG. 10.—Absorption curves showing the structure of GR-S in the absence of modifier.

little hope that these methods will detect such differences, since the fundamental structure is so similar. The differences in physical properties evidently result either from a variation in a relatively small proportion of the chemical linkages, as might readily be the case for cross-linking, or in variations which do not give rise to unique absorption bands. The amount of modifier present is so small that it does not appear directly in any of the absorption curves.

Since unmodified copolymers of butadiene and styrene are generally insoluble in organic solvents, films were made from latices of the copolymers containing little or no modifier. The absorption curves for these are shown in Figure 10, respectively for samples containing 0.1 per cent mercaptan activator-modifier and 0.1 per cent mercaptan activator. The latter activator is considered to have little or no modifying action. The increased number of side vinyl groups compared to GR-S becomes apparent from the increased absorption of the 996 cm^{-1} band. This increase is more pronounced for the slightly modified sample than for the one which contained activator only. This evidence is far from conclusive as the effect of the modifier and activator on the amount of 1,2-polymerization, but indications are that when the normal amount of modifier is used there are fewer side vinyl groups formed than if no modifier or only a very slight amount of modifier is present.

RESUMÉ

The physical properties of a synthetic polymer are associated with variations in molecular structure which depend on the conditions of the polymerizing reaction and the monomers used. In some cases, structural differences of significance for physical properties cannot be detected by infrared methods because the relative number of chemical linkages affected is too small. An important structural detail which can be followed by infrared analysis is the relative amount of 1,2 and 1,4-polymerization occurring in polymerization reactions of butadiene. Absorption curves are reproduced to show the wide range in the relative amounts of these two structures. A description is given of an attempt to obtain a quantitative measure of this ratio by means of a calibration curve derived from known mixtures of pure 1-octene and 2-octene. For polyisoprene, variations in the proportions of 1,4 and 1,2 or 3,4 structure also occur, depending on the type of polymerization. Comparison with Hevea rubber and Balata fails to disclose definite evidence of *trans*-isomerism in synthetic polyisoprene. Structural differences due to oxidation of polymers may be readily apparent in infrared spectra, hydroxyl and carbonyl groups being especially prominent. The effectiveness of antioxidant in preventing structural changes caused by oxidation is shown in a series of absorption curves for samples of GR-S with and without antioxidant. When the samples were heat-treated in air, pronounced structural changes occurred in the sample without antioxidant, but no perceptible changes were evident in the sample with antioxidant. On the other hand, the antioxidant used (phenyl-β-naphthylamine) was ineffective in stabilizing the structure toward ultraviolet light.

ACKNOWLEDGMENT

We wish to express our appreciation to L. B. Sebrell and The Goodyear Tire & Rubber Company for permission to publish this work, to A. M. Borders and J. O. Cole of the Research Staff for preparing the polymers used, and to M. R. Fenske for supplying the samples of 1-octene and 2-octene.

REFERENCES

[1] Alekseeva, *Zhur. Obshchei Khimii U.S.S.R.* **11**, 353, 358 (1941); RUBBER CHEM. TECH. **15**, 693, 698 (1942); Thompson and Torkington, *Trans. Faraday Soc.* **41**, 246 (1945); unpublished work of M. W. Swaney, J. U. White and P. J. Flory, Esso Laboratories, Standard Oil Development Co., unpublished work of R. S. Rasmussen and R. R. Brattain, Shell Development Co.

[2] Tuot, Lecomte and Lorillard, *Compt. rend.* **211**, 586 (1940); Thompson and Torkington, *Trans. Faraday Soc.* **41**, 246 (1945); unpublished work of M. W. Swaney, J. U. White and P. J. Flory, Esso Laboratories, Standard Oil Development Co.

[3] Hendricks, Wildman and Jones, *Arch. Biochem.* **7**, 427 (1945).

[4] Naylor, *Trans. Inst. Rubber Ind.* **20**, 45 (1944); Bloomfield, *India-Rubber J.* **108**, 495 (1945).

THE PROPORTION OF CRYSTALLINE AND AMORPHOUS COMPONENTS IN STRETCHED VULCANIZED RUBBER *

A. J. WILDSCHUT

RUBBER-STICHTING, DELFT, HOLLAND

1. INTRODUCTION

Since Katz[1] recognized the crystalline structure in stretched rubber, x-ray analysis has improved our knowledge about high polymeric elastic substances to a considerable extent. The influence of temperature on the behavior of the rubber crystallites has been studied on raw as well as on vulcanized rubber. Various influences of mixing and vulcanization on the x-ray pattern have been investigated. The fibrous character of stretched rubber has been definitely established, and this has contributed considerably to the important new theories about high elasticity.

Long before the crystallinity of stretched and of "frozen" rubber was proved by the x-ray diagram, it was understood that physical properties, such as specific weight, hardness, light-transmission, show transition points when their courses with temperature are determined. It has been known for a long time that stored raw rubber can become hard and opaque, while the original suppleness can be restored by heating or even by repeated bending and stretching. Bunschoten[2] pointed out that the specific gravity of "frozen" raw rubber decreases considerably after heating, and increases again after the rubber is kept for a certain time at a relatively low temperature. Though the possibility of a phase-change was considered, the "freezing" of rubber was not then explained by assuming a partial crystallization. In later years analogous experiments, though over a much longer range of temperature, were carried out by Bekkedahl[3], who found several transition points in the specific volume-temperature curve.

Many other investigations could be mentioned in this connection, but those two suffice to show that x-ray analysis is not the only way in which the crystallization of rubber can be studied. After recognizing the importance of crystallization on the plastic properties of vulcanized rubber[4], the author made a study of the relation between elastic tension and temperature, which relation appeared also to be influenced by crystallization to a considerable extent. Though originally meant for a different purpose, this study proved to be valuable also for a quantitative investigation of the crystallization. It appeared possible to calculate the percentage of crystalline material in stretched vulcanized rubber from tension-temperature relations as determined for thermodynamical investigations.

It is not the author's intention to deal with these latter investigations[5] in full, as this is quite a different subject. Only the side path, leading to a new method of quantitative determination of the degree of crystallization, will be treated here.

* Reprinted from the *Journal of Applied Physics*, Vol. 17, No. 1, pages 51–60, January 1946. This is Communication No. 51, Rubber-Stichting, Delft, Holland.

2. THE TENSION–TEMPERATURE RELATION

The well-known thermodynamical formula:

$$\sigma = (\partial U/\partial L)_T + T(\partial\sigma/\partial T)_L \qquad (1)$$

where σ is the elastic tension, U the internal energy, L the length, and T the absolute temperature, used already by Wiegand and Snyder[6], denotes a linear relation between the tension σ and the temperature T. The scope of the $\sigma - T$ line fixes $(\partial\sigma/\partial T)_L$, while the point of intersection with the ordinate gives the value for $(\partial U/\partial L)_T$.

This formula is valid provided the process is reversible. Therefore the rubber sample under investigation must be sufficiently elastic so that plastic flow during the measurements may be neglected. With a normal vulcanized pure-gum mixture from natural rubber it is comparatively easy to meet this requirement. If such a rubber is stretched, heated for some time at, for example, 70° C till the rate of relaxation is sufficiently small, cooled down to room temperature, and heated again to 70° C, as has been done by Meyer and Ferri[7], the original tension is reached again or is so nearly approximated that the difference may be neglected. As the process is reversible, Equation (1) is valid and the relation found between tension and temperature must be linear. Up to a certain extent the experimental data are in accord with the thermodynamical theory, but for a complete explanation of all experimental facts it appeared necessary to consider a possible partial crystallization of the rubber investigated. This crystallization is influenced also by the velocity with which the experiments are carried out.

3. METHOD OF DETERMINING THE TENSION–TEMPERATURE RELATION

The apparatus (see Figure 1) comprises a part regulating the temperature of the test-piece and a part by means of which the elastic tension can be measured at constant elongation. As it was believed desirable to heat the rubber in air, a double-walled glass-mantle, through which a liquid could be pumped,

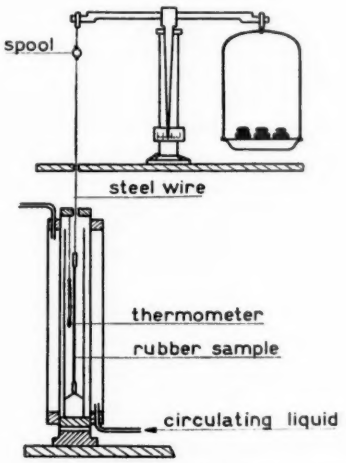


FIG. 1.—Apparatus for determining the tension-temperature relation.

was constructed around the test-piece, while the tension was measured by means of an ordinary balance from which one of the scales had been removed. The elongation was determined and controlled by measuring the distance of two marks on the rubber by means of two calibrated glass plates, acting as cathetometer.

The stretched rubber was even more sensitive to slight fluctuations in temperature than the precision-thermometer used. By means of two water baths, however, one for heating and cooling and the other for measuring at constant temperature, the temperature inside the mantle could be kept sufficiently constant.

Small variations in elongation of the part of the test-piece between the marks could occur, as this part was not always elongated in the same way as the rest of the test-piece. This could then be corrected by means of a small spool in the steel wire connecting the sample with the balance.

The cross-section of the test-pieces used was mostly about 0.5 sq. mm. (e.g., 0.3×1.4 mm.); the loads varied up to about 200 grams and could be measured with an accuracy of 0.1 gram.

Originally the experiments were carried out over a range from room temperature to 70° C, but in the course of the investigations it proved to be necessary to extend this range up to 100° C and down to −10° C. For temperatures below room temperature, alcohol, cooled in a mixture of solid carbon dioxide and acetone, was pumped through the glass mantle.

Most experiments were carried out after heating the stretched rubber at 70° C during 4 hours. The sample was then cooled down in steps of about 10 degrees Celsius. At each temperature the rubber was kept for about 10 minutes.

If the sample was heated to temperatures above 70° C, the time of relaxation, at least in the cases of higher elongations, had to be shorter than four hours, as otherwise breaks might occur. As the rate of relaxation increases strongly with increasing temperature, no difficulties were presented by this.

4. INFLUENCE OF CRYSTALLIZATION

If stretched and heated vulcanized rubber is cooled down again, three cases can be distinguished, dependent on elongation and rate of cooling. Examples of these cases are given in Figure 2.

First case, Fig. 2A.—Low elongation (208 per cent). There is but little crystallization, and after having been kept at 70° C during 4 hours, the rubber is certainly amorphous. On cooling, the amorphous state can be maintained and in that case the tension-temperature relation is straight, in accordance with Equation (1). On heating, the initial point is reached again, proving that relaxation during the cycle may be neglected.

Second case, Fig. 2B.—Medium elongation (357 per cent). The rubber crystallizes on stretching, but after 4 hours at 70° C the sample may be considered amorphous. On cooling, the tension decreases linearly with temperature to the transition point of 36° C. Then partial crystallization sets in, causing a marked increase in the slope of the tension-temperature line, which, however, remains straight.

Third case, Fig. 2C.—High elongation (607 per cent). The stretched sample is partly crystallized, and 70° C is too low to melt the crystallites under these circumstances. On cooling, a straight line without a transition point is obtained, as over the whole range the sample is already (partly) crystallized.

The increase in degree of crystallization, which certainly takes place on cooling, increases the slope of the line but apparently does not influence the linear course of the tension-temperature relation.

From Figure 2B it can be seen clearly that the tension of partly crystallized rubber is lower than it would be if no crystallization had taken place. This latter situation can easily be realized if the rubber is cooled down comparatively rapidly, as has been done by Meyer and Ferri[7], who had their test-pieces in direct contact with the cooling medium, water. This is the reason why these investigators could not observe a transition point.

On heating again a retardation in the melting of the crystallites occurs, with the effect that partial crystallization still exists, even in the range above the melting point. The observed lower tensions are a consequence of this retarda-

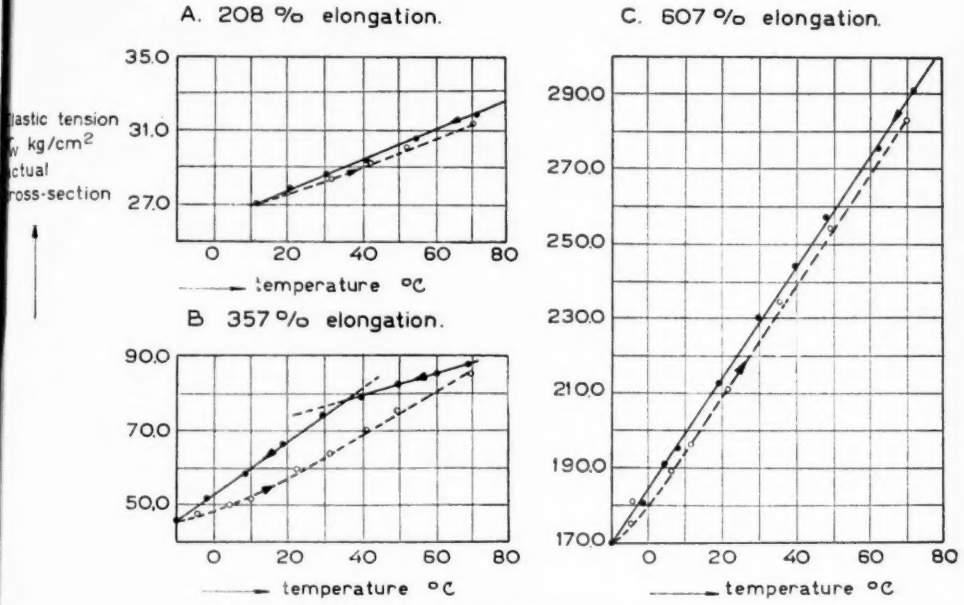


FIG. 2.—Tension-temperature diagrams of vulcanized natural rubber (see Reference *a* of Table I) at different elongations.

tion, since they cannot be caused by relaxation. Ultimately the initial tension is practically reached again, which gives proof that relaxation may be neglected.

At high elongations very little retardation appears to occur (Figure 2C). The reason for this phenomenon is not clear as yet. Also in this case the initial tension is approximated sufficiently to justify neglect of relaxation.

5. THE "MELTING POINT" OF THE CRYSTALLITES

It was learned from measurements at medium elongations that the transition point in the $\sigma - T$ curve was displaced to higher temperatures when higher elongations were used. Therefore it was logical to search for the missing transition points at higher elongations by measuring over a wider range of temperature. For this purpose the initial point was raised to 90° C and later even to

100° C. At elongations of about 600 per cent breaks often occurred, but sufficient relaxation was obtained in a short time, *e.g.*, 15 minutes. Although the initial tension is not quite reached again (see Figure 3A), the influence of relaxation during the cooling may still be neglected, as at lower temperatures the rate of relaxation decreases strongly.

As the curve of Figure 3A shows no transition point, heating for 15 minutes at 100° C is not sufficient to melt a noticeable part of the crystallites. After

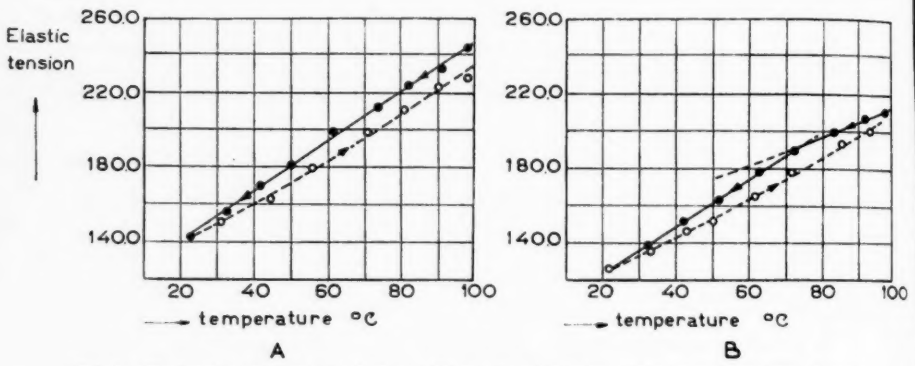


FIG. 3.—The tension-temperature relation at 600 per cent elongation. Influence of the time of heating. Natural rubber pure-gum vulcanizate (see Reference *a* of Table I). *A*. Heated 15 minutes at 100° C. *B*. Heated 60 minutes at 100° C.

heating for 60 minutes, however, the transition point appears at about 74° C (Figure 3B). From further contemplations it can be derived that in this case by heating at 100° C during 60 minutes about 60 per cent of the crystalline phase is melted.

So it is clear that at higher elongations not only a high temperature but also a comparatively long time is needed to melt the crystallites. On cooling, crystallization sets in at a fairly definite point; there is only a small range of

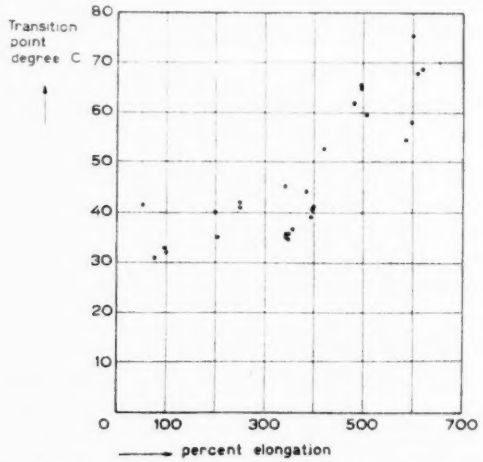


FIG. 4.—Transition points in the $\sigma - T$ relation as a function of the elongation. Natural rubber pure-gum vulcanizate (see Reference *a* of Table I).

temperature during which crystallization begins. After that range has been passed, the percentage of crystalline material appears to increase in inverse proportion to temperature (see Section 6). The rather sharp solidification point may be caused by the existence of crystallization nuclei or small crystallites acting as nuclei.

Since the melting of the crystallites appears to depend so strongly on circumstances, it is not astonishing that no distinct relation between transition points and elongation could be derived from the experimental data. Yet, when the results of twenty-six measurements are plotted on squared paper, as has been done in Figure 4, it is clear that a certain relation is present.

An increase in elongation from 300 to 600 per cent corresponds to a displacement of the transition point from about 40 to about 65° C.

These measurements provide us with a qualitative picture of the influence of crystallization on the tension-temperature relation. The most important conclusion is that the linear course of this relation is not disturbed by increasing partial crystallization.

6. DETERMINATION OF THE DEGREE OF CRYSTALLIZATION

In Figure 5 the course of tension with temperature at medium elongation, as given already in Figure 2B, is pictured again.

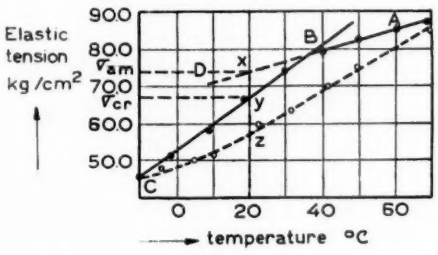


FIG. 5.—Calculating the degree of crystallization from the tension-temperature relation. (Natural rubber pure-gum vulcanizate (see Reference a of Table I) at 357 per cent elongation.)

The rubber has been stretched, heated for 4 hours at 70° C, and then cooled down comparatively slowly. The stretch *AB* corresponds with wholly amorphous rubber (see below) and is thus in accordance with Equation (1). Below the transition point at *B* partial crystallization occurs. The stretch *BC* therefore corresponds to partial crystallized rubber with increasing amount of crystalline material. The slope of this part of the curve is caused by the combination of the decrease according to form, (1), known to be linear, and the decrease, caused by the growing amount of crystalline material. The result is a linear decrease of tension with temperature; therefore the decrease, caused by the crystallization effect, must also be linear.

Now this decrease is caused by the fact that decreasing temperature causes an increasing amount of crystalline material, while more crystallization involves a lower tension. As the combination of these two functions is linear, it is very likely that both of them are linear also. If that is so, the conclusion would be reached that the elastic tension decreases in inverse proportion to the amount of crystalline material.

Presuming this conclusion valid, the calculation of the degree of crystallization in stretched vulcanized rubber from measurements as given in Figure 5 is very simple.

If no crystallization had taken place, the tension-temperature relation would have followed the course *BD* and at 20° C point *X* would be passed, corresponding with an "amorphous tension", σ_{am}^{20}, of 73.7 kg. per sq. cm. Since, however, the rubber is partly crystallized, at 20° C point *Y* is reached, corresponding to a "crystalline tension", σ_{cr}^{20}, of 66.9 kg. per sq. cm. This tension is 9.2 per cent lower than the "amorphous tension," which denotes that 9.2 per cent of the rubber molecules have been eliminated by crystallization.

In general, the percentage of crystalline material *K* is given by:

$$K = \frac{\sigma_{am} - \sigma_{cr}}{\sigma_{am}} 100 \qquad (2)$$

The tension in stretched rubber is thus caused only by the amorphous phase. Only these molecules have a possibility to return to their most probable position; as soon as they have entered a crystal lattice, this possibility no longer exists.

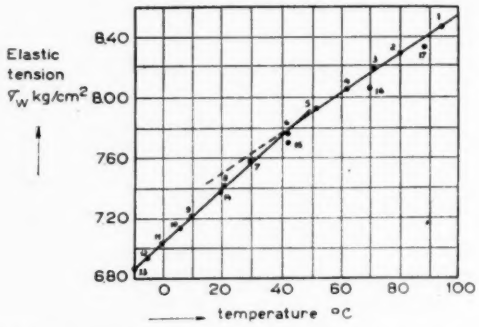


FIG. 6.—Existence of crystallization in stretched vulcanized rubber (see Reference *a* of Table I) at 55 per cent elongation.

If after cooling to −10° C, the test-piece is heated again, the tension at 20° C corresponds to that of the point *Z* (see Figure 5). On passing *Z*, a higher degree of crystallization still exists, but this situation is not stable and is, therefore, left out of account. It denotes, however, the necessity to consider always the history of a given piece of rubber if its crystallization is to be measured.

Only if it is certain that at the initial point *A* the rubber is wholly amorphous, exact data about the degree of crystallization are obtained, for the transition point may appear also when at higher temperatures the rubber is still partly crystallized. In those cases only an increase in degree of crystallization is found, and the total amount of crystalline material may be higher.

It is, however, rather simple to prove the presence of the wholly amorphous state above the transition point. If the rate of cooling is augmented, the "crystalline part" of the tension-temperature line becomes curved—for crystallization takes time—while the "amorphous part", if wholly amorphous, remains straight. In this way it has been proved that, in cases as pictured in Figure 5, the test-piece must have been wholly amorphous at 70° C.

Theoretically the "crystalline part" of the tension-temperature curve cannot be straight, since crystallization is dependent on time, but since this relation is logarithmical, it suffices to measure with the velocity described in Section 3 to get a line that cannot be distinguished from a straight one.

With x-ray measurements below 300 per cent elongation, no crystallization is observed in natural rubber pure-gum mixtures. By means of the method described above, however, the existence of crystallization effects can be shown, and the amount of crystalline material can be calculated at elongations as low as 50 per cent. The degree of crystallization is then naturally very small, about 1 per cent, but the effect is unmistakable, as is shown in Figure 6.

As yet it has not been possible to control all factors influencing crystallization at lower elongations. Sometimes crystallization occurs, but in other cases it may not happen at the same or even higher elongations. An example of this has already been given in Figure 2A. The degree of crystallization found varies also in separate cases. But this is not considered essential at this stage of the investigations. Stress can be laid on the conclusion that at these low elonga-

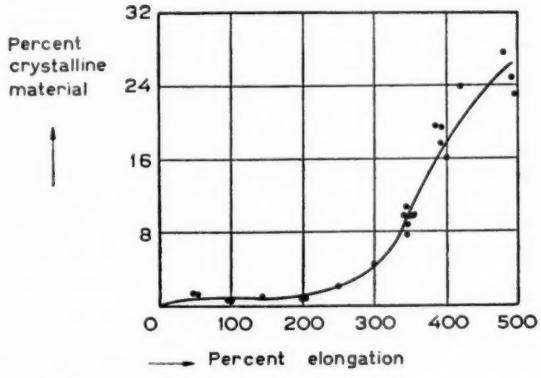


FIG. 7.—Percentage of crystalline material in stretched vulcanized natural rubber (see Reference *a* of Table I) at 20° C.

tions a distinct, though very small, crystallization effect occurs. Whether at 50 per cent elongation an exact degree of crystallization can be determined at all is not certain, since it is possible that this degree varies according to circumstances, and factors depending on the laws of probability may also play a part.

The degrees of crystallization, calculated from 25 measurements on a natural rubber pure-gum mixture (different vulcanizates, but always the same mixture and cure), are given in Figure 7 as well as in Table I.

As soon as the rubber is elongated, crystallization sets in, but up to 250 per cent not more than 2 per cent is crystallized. Above 300 per cent elongation crystallization increases rapidly, till at 500 per cent a maximum of about 27 per cent of crystalline material is reached. By extrapolating the curve of Figure 7 to 600 per cent elongation, the maximum degree of crystallization can be estimated to be about 30–32 per cent. So even in that case the amorphous phase predominates.

Presuming that at 600 per cent elongation, 30 per cent of the stretched rubber is crystallized, it is possible to gain complete insight in Figure 3B. When passing at 20° C from the extrapolated upper part of the curve to the lower

TABLE I

PERCENTAGE OF CRYSTALLINE MATERIAL IN STRETCHED VULCANIZED RUBBER[a] AT INCREASING ELONGATION (20° C)

Percentage elongation	Percentage of crystalline material	Percentage elongation	Percentage of crystalline material
50	1.4	347	8.6
55	1.3	350	9.5
97	0.5	357	9.2
100	0.5	385	19.6
120	0.9	390	12.6
200	0.9	392	17.7
205	0.8	397	19.3
250	2.0	400	16.0
300	4.3	420	23.8
342	9.7	480	27.4
342	8.3	492	24.5
345	10.4	495	22.8
345	7.5		

[a] Composition: crepe rubber 100, diphenylguanidine 0.5, mercaptobenzothiazole 0.8, sulfur 1.75, zinc oxide 5.0, stearic acid 1.0, aldol-α-naphtylamine 1.0. Cure 20 minutes at 142° C in a press.

part, the tension decreases from 148.4 to 122.7 kg. per sq. cm., that is, with 17.4 per cent. If the upper part had represented the wholly amorphous state, the decrease would have been 30 per cent. So $17.4 \cdot 100/30.0 = 58$ per cent of the crystalline phase was melted by heating at 100° C during an hour.

Of course in such a calculation this exactness has no sense, but the conclusion may be drawn that rather more than half of the crystalline phase will be melted in an hour and that it will take at least another hour to reach the wholly amorphous state. Unfortunately most samples cannot stand this, so 600 per cent is about the natural limit for this sort of investigation. Perhaps an improvement can be made by heating the unstretched sample at 100° C and then elongating it; these experiments will be done in due course.

7. INFLUENCE OF TEMPERATURE ON DEGREE OF CRYSTALLIZATION

Since the relation between tension and temperature is linear, a tension coefficient at constant elongation, $(\partial\sigma/\partial T)_L$, can be calculated from these measurements. As long as the rubber is amorphous, the value of this tension coefficient depends only on the elongation. Below the transition point the tension coefficient increases, for the increasing degree of crystallization causes an additional decrease in tension. The "crystalline tension coefficient" therefore depends on time in the same way as the crystallization itself[4].

The degree of crystallization can be calculated from the tension coefficients and the transition temperature as follows:

From Figure 5 it can be seen that the tension of the transition point, σ_T, is given by:

$$\sigma_{T_s} = \sigma_{T,\mathrm{am}} + (\partial\sigma_{\mathrm{am}}/\partial T)_L(T_s - T) \tag{3}$$

as well as by:

$$\sigma_{T_s} = \sigma_{T,\mathrm{cr}} + (\partial\sigma_{\mathrm{cr}}/\partial T)_L(T_s - T) \tag{4}$$

where $\sigma_{T,\mathrm{am}}$ and $\sigma_{T,\mathrm{cr}}$ are, respectively, "amorphous" and "crystalline" tensions at a temperature T and $(\partial\sigma_{\mathrm{am}}/\partial T)_L$ and $(\partial\sigma_{\mathrm{cr}}/\partial T)_L$ are the tension coefficients for the wholly amorphous and partially crystallized rubber, respectively.

If the values for $\sigma_{T,\text{am}}$ and $\sigma_{T,\text{cr}}$, derived from Equations (3) and (4), are substituted in Equation (2), we get:

$$K_T = \frac{[(\partial\sigma_{\text{cr}}/\partial T)_L - (\partial\sigma_{\text{am}}/\partial T)_L](T_s - T)}{\sigma_{T_s} - (\partial\sigma_{\text{am}}/\partial T)_L(T_s - T)} 100 \qquad (5)$$

from which the percentage of crystalline material K_T can be calculated at any temperature T. Equation (5) can be written $xy + ax + by - c = 0$, which is an equation of a hyperbola. As can be seen from Figure 8, in practice the relation between K_T and T is approximately linear, as long as short ranges are considered.

The amounts of crystalline material have been calculated for the elongations 357 (the case represented in Figure 5) and 492 per cent; the results are given in Figure 8.

The straightness of the tension-temperature curve has been proved down to $-10°$ C. Below this temperature, calculation of K_T from Equation (5) has little or no physical meaning. In the first place the rate of crystallization diminishes at decreasing temperature so strongly that for this reason alone it is doubtful whether the percentages represented by the dotted part of the curve

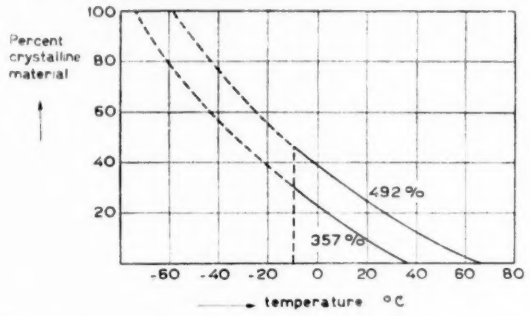


FIG. 8.—Percentage of crystalline material as a function of temperature. Natural rubber pure-gum vulcanizate (see Reference *a* of Table I).

are ever reached at all. Secondly Equation (5) is only valid as long as the "crystalline part" of the $\sigma - T$ curve remains straight as well as continuous. Any change in modification causes a break in the $\sigma - T$ curve. This makes an extrapolation below the temperatures of the measurements without physical significance.

The degree of crystallization appears to be strongly dependent on temperature. While at room temperature (20° C) the maximum percentage crystalline material may be estimated to be about 30 per cent, at zero degrees this maximum may be 45 per cent and at $-10°$ C even as high as 50 per cent. The highest temperature at which crystallization in stretched rubber exists appears to be about 80° C, a conclusion that can be derived also from Figure 4. Above 60° C the amount of crystalline material remains below 10 per cent, provided the situation is stable. Of course, if stretched rubber is heated rather rapidly, higher degrees may temporarily occur, but then the system is not in equilibrium.

8. COMPARISON WITH X-RAY MEASUREMENTS

Quantitative measurements of the crystallization in stretched vulcanized rubber by means of the x-ray method have been done by Field[8] and by Goppel[9].

Both investigators compared the intensities of the diffuse rings in the diagrams of amorphous and partly crystallized rubber, while also measurements of the intensities of the diffraction spots were done.

It lies beyond the scope of this paper to discuss these investigations in full. As it happens, however, the results of Field and of Goppel show a large difference: while the former finds at 500 per cent elongation and at room temperature a degree of crystallization of 65–70 per cent, the latter measures 25–30 per cent, which is in accordance with the results of the thermodynamical method described above.

The work of Goppel was carried out independently of that of the author and most of it at an earlier date. His results as given in Figure 9 are obtained on the same mixture on which the thermodynamical measurements have been done, but also various other pure-gum mixtures have been investigated[10], and it appeared that the differences between them were small.

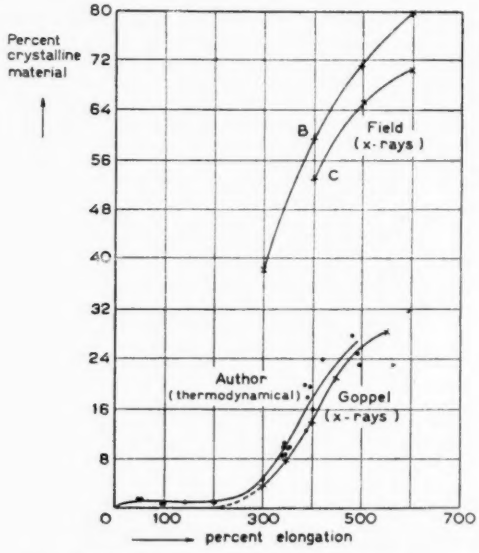


FIG. 9.—Crystallization in stretched vulcanized rubber (see Reference 10) according to three investigations.

Results of both x-ray investigation, as well as the results obtained with the thermodynamical method, have been collected in Figure 9.

There is a close agreement between the results of Goppel and those of the author, while the data given by Field diverge very considerably. It is most unlikely that this is caused by the comparatively small differences in mixture and cure, but it is not yet possible to state the exact cause of this phenomenon.

Various arguments can be advanced for the existence of not more than a moderate amount of crystalline material in stretched vulcanized rubber. It is unlikely that an entangled knot, with primary valency bonds between the molecules, can be stretched in such a way that a great amount of regularity is gained. As soon as certain parts of the chains have entered into crystal lattices, other parts are hindered in their movements and less able to do the same. The primary valency bonds caused by vulcanization arise while the

rubber is unstretched; by stretching some of these bonds may break, but others do not. It is in contravention of probability that the irregular network can be transferred in a system of crystal lattices; so crystallites can be formed only to a limited amount.

The thermodynamical measurements can only be compared with the two x-ray investigations mentioned. One is in close agreement with them, the other diverges largely. A third, if possible independent, measurement of the degree of crystallization will be required to make certain where the truth lies.

9. GENERAL PICTURE OF STRETCHED VULCANIZED RUBBER

The author is inclined to believe that the lower figures for the amount of crystalline material in rubber are right. This leads to the assumption that stretched vulcanized rubber is composed of an amorphous phase, with up to a third part crystallized material. The existence of crystallization is important as an indication of regularity, but it is doubtful whether crystallization, in itself, is of paramount importance for the tensile strength of rubber.

Immediately after elongation begins, orientation of the rubber molecules occurs. This orientation is one of the main causes of the formation of a high mechanical firmness during elongation. Crystallization, though directly important for certain other properties, is only an incidental phenomenon, and it is not even certain whether the existence of crystallites adds to the tensile strength or not. At any rate high tensile strength is very easily possible without any crystallites playing a role, even in pure-gum vulcanizates. At temperatures up to 100–140° C, vulcanized rubber keeps its tensile strength completely[11], while certainly under these circumstances no crystallization is present.

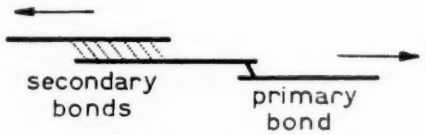


FIG. 10.—On the mechanism of break.

Of equal importance with regard to the tensile strength may be the way the secondary forces between the molecules decrease at increasing mutual distance. If this function is favorable, a high tensile strength may occur even at medium orientation.

It is not likely that the primary valency bonds in vulcanized rubber are decisive for tensile strength. They are, of course, important with regard to plastic flow, but it is unlikely that, on stretching, they are responsible for equal parts of the tension. So in the region shortly before break, these primary bonds may be broken one after another, if the combined secondary energies between two chain-parts, drawn parallel, are higher than the energy of the primary bond concerned. (Compare Figure 10.)

The tensile strength is caused mainly by secondary forces, added systematically along the chains. This addition is possible for secondary forces only[12]. The crystallites may exert additional forces on the surrounding amorphous phase and thus add to modulus and tensile strength, in the same way that carbon black in Perbunan does, but it is likewise possible that this effect—if it exists at all—is overcompensated by the partial elimination of rubber

molecules by crystallization (which causes, as has been shown above, a decrease in elastic tension). Of course the crystallites in themselves are firmly bound together, but this is of no importance to the tensile strength, as they are embedded in amorphous material. This may be the most important conclusion from our measurements about the degree of crystallization: when determining the tensile strength the forces are applied on an amorphous phase and not on a bundle of crystals.

This vision of the situation in stretched vulcanized rubber is strengthened by various phenomena, observed on synthetic rubbers[5], with and without carbon black. Synthetic rubbers with very weak pure-gum mixtures show a normal high tensile strength when carbon black is added: secondary forces must play a role. Lightly swollen rubber[13] has lost most of its mechanical firmness; after evaporation of the swelling liquid the original tensile strength is completely restored. This phenomenon can be explained only by presuming secondary forces to be responsible for the tensile strength.

More could be said about this, but that would carry us much too far. It does not lie within the scope of this article to discuss all physico-chemical aspects of the rubber molecule, but only to draw attention to the fact that a relatively low degree of crystallization is likely to exist and that it leads to an essentially different picture of stretched rubber from that of a high degree. The picture, corresponding to a low degree of crystallization, agrees better with phenomena observed with synthetic rubbers.

SUMMARY

Determinations of the tension-temperature relation of stretched vulcanized rubber can provide us with data about the proportion of crystalline and amorphous components. The amount of crystalline material appears to be 30–32 per cent at 600 per cent elongation and at 20° C. An expression is derived relating percentage of crystalline material and temperature. The results are in close agreement with those of x-ray measurements carried out by Goppel, but diverge largely from those obtained by Field. The cause of this difference is not yet clear. Stretched vulcanized rubber consists of a predominating amorphous phase, with crystallites embedded in it. On stretching orientation occurs, and a systematic addition of secondary valency forces is possible. This is the main cause of the existence of a certain tensile strength. Crystallization, though important as an indication on orientation, is more or less an incidental phenomenon. The distance function of the secondary forces may be of equal importance with the orientation.

REFERENCES

[1] Katz, *Kolloid-Z.* **36**, 300 (1925).
[2] Bunschoten, *Versl. Meded. Afd. Handel Dep. Landb. Nijverh. Handel*, **1921**, No. 6.
[3] Bekkedahl, *J. Research Natl. Bur. Standards* **13**, Sept. 1934.
[4] Wildschut, *Physica* **10**, 571 (1943); *Rev. gén. caoutchouc* **21**, 9 (1944).
[5] A survey is made by Wildschut in "Technological and Physical Investigations of Natural and Synthetic Rubbers", Elsevier Publishing Co., Amsterdam, **1945**.
[6] Wiegand and Snyder, *Trans. Inst. Rubber Ind.* **10**, 234 (1934).
[7] Meyer and Ferri, *Helv. Chim. Acta* **18**, 570 (1935).
[8] Field, *J. Applied Physics* **12**, 23 (1941).
[9] Goppel, "Quantitatieve Rontgenografische Onderzoekingen aan Rubber", Thesis, Delft, **1945**.
[10] The results of Goppel and the present author have been obtained on the vulcanizate defined in Note *a* of Table 1. The data of Field have been derived from his Figures 10 and 11. *Compound B:* smoked sheet rubber 100, sulfur 2, piperidinium pentamethylenedithiocarbamate 2, zinc oxide 2; cured 10 minutes at 127° C. *Compound C:* smoked sheet rubber 100, sulfur 2, Zimate 1, zinc oxide 1; cured 20 minutes at 127° C.
[11] Van Rossem and Van Der Meijden, *J. Soc. Chem. Ind.* **45**, 67T (1926); Somerville and Russell *Ind. Eng. Chem.* **25**, 1096 (1933).
[12] See also Briegleb, "Zwischenmolekulare Kräfte und Molekülstruktur", Sammlung Chemischer und Chemisch-technischer Vorträge, New Edition, **1937**, No. 37.
[13] A swelling of 8-10 volume—per cent is sufficient.

SIGNIFICANCE OF THE EQUATION OF STATE FOR RUBBERS *

EUGENE GUTH, PAUL E. WACK, AND ROBERT L. ANTHONY

POLYMER PHYSICS LABORATORY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA

INTRODUCTION

The physical significance and the molecular interpretation of equations of state for gases, liquids, and solids are well known. The equation of state for a gas may be given in the form:

$$p = p(V, T) \tag{1}$$

where p is the pressure, V the volume, and T the absolute temperature. The equation of state for a solid, which is deformed unilaterally, may be obtained from Equation (1) by replacing p by $(-Z)$, the (nominal) stress (=force per unit original cross-section) and V by ϵ, the strain (=extended length divided by original length minus one):

$$Z = Z(\epsilon, T) \tag{2}$$

A stress-strain curve:

$$Z = Z(\epsilon) \tag{2a}$$

is the *isothermal* obtained from Equation (2) at constant temperature T. A stress-temperature curve:

$$Z = Z(T) \tag{2b}$$

is the *isometric* obtained from Equation (2) at a constant extension ϵ. An extension-temperature curve:

$$\epsilon = \epsilon(T) \tag{2c}$$

is the *isotonic* obtained from Equation (2) at a constant stress Z. Equations (2a), (2b), and (2c) are, of course, equivalent. For certain solids, the isothermals or the isometrics or the isotonics may be obtained experimentally in a direct way.

For rubber, none of the "iso"-curves may be obtained directly. For instance, time is needed to take an isothermal, a stress-strain curve. During this time the stress relaxes by an amount which depends on the conditions under which the curve is taken. The purpose of the present paper is to clarify the role of the time element in the various methods for obtaining the equation of state.

STRESS–STRAIN CURVES

Apparently the simplest way to obtain the equations of state consists in the taking of stress-strain curves at various temperatures. Unfortunately, the time element needed for this procedure may mask or even reverse the correct dependence of stress on temperature. Stress-strain curves taken at slow constant rates of loading or stretching yield on cross-plotting at constant

* Reprinted from the *Journal of Applied Physics*, Vol. 17, No. 5, pages 347–351, May 1946.

strain a decrease of the stress with increasing temperature, in contradiction to the kinetic theory of rubber electricity[1].

For fast stress-strain curves the correct dependence, *i.e.*, increase, of the stress on the temperature is obtained. Figure 1 shows stress-strain curves at various temperatures obtained with the fast stress-strain apparatus[2], developed

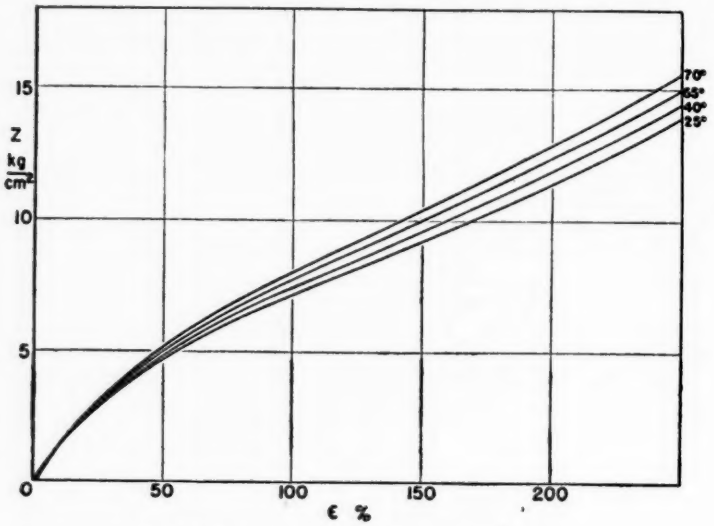


FIG. 1.—Stress-strain curves for various temperatures.

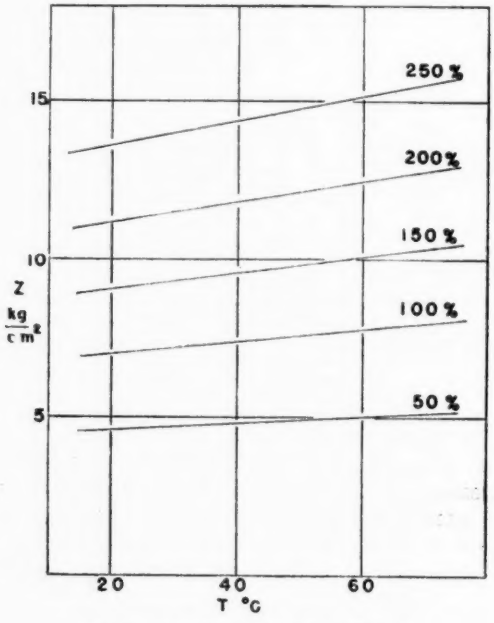


FIG. 2.—Isometrics derived from Figure 1.

in the Polymer Physics Laboratory at Notre Dame. Figure 2 shows isometrics which resulted from Figure 1 on cross-plotting; they exhibit the increase of stress with increasing temperature.

This method alone, however, cannot give a reliable equation of state. For, it is not *a priori* known how fast[3] the stress-strain curve has to be taken to give the "correct" dependence of the stress on the temperature. In addition, the adjective "correct" needs further elaboration. At any rate this method would have to be supplemented by a study of the effect of the speed of stretching on the stress-strain curve.

ISOMETRICS BY RELAXATION METHOD

The relaxation method of obtaining isometrics operates as follows. A sample is kept at constant extension at a constant temperature T^* for the time interval t^*. The stress relaxes as shown in Figure 3. Then the temperature

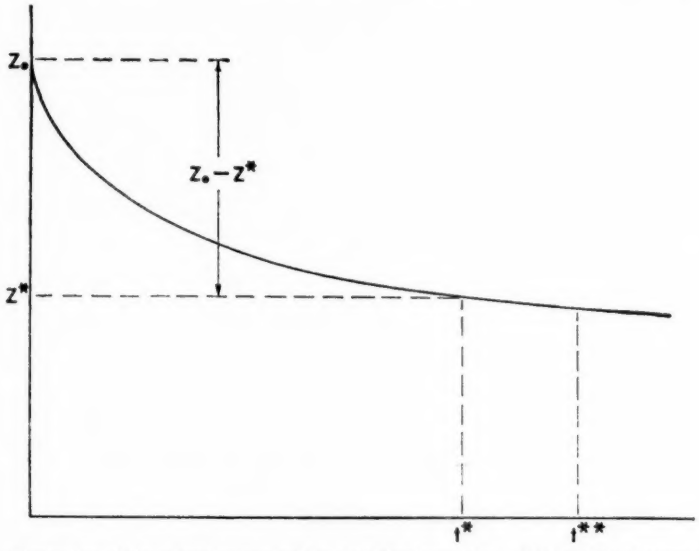


FIG. 3.—Illustration of the relaxation method for obtaining isometrics. Z_0 is the initial stress at $t = 0$.

is lowered and the change in stress is measured, giving the desired isometrics as indicated in Figure 4.

The time t^* is chosen so that in the time interval $(t^{**} - t^*)$ (cf. Figure 3) needed to take the measurements over the temperature interval $T^* - T^{**}$ (*cf.* Figure 4) the amount of stress relaxation is within the experimental error.

In earlier work it was customary to take measurements from T^{**} back to T^* also and call the isometrics reversible or equilibrium curves, if the branch coming back coincided with that going down. This is unnecessary, however. Suppose one has chosen t^* so that no measurable stress relaxation takes place going down from T^* to T^{**}, that is, for the time $(t^{**} - t^*)$, but that stress relaxation is not negligible for the interval $2(t^{**} - t^*)$ needed to cover also the return T^{**} to T^*. Then, when coming back, one would obtain the dotted line in Figure 4. For thermodynamic computations one still may use the branch on going down. This statement will be obvious after considering the theory of the relaxation method of obtaining isometrics in the following sections of this paper.

Apart from the clarification of this item, there were other important points left somewhat obscure. In the actual experiment all rubbers show some (permanent or temporary) set, when the stress is released, after the isometrics are taken. Should one take this final unstretched length or the initial one (before the experiment started) in computing the extension ϵ? Meyer and Ferri[4], for instance, have used the final length. Our theory shows that the initial length should be taken instead. In previous work (Meyer and Ferri[4], our own work[5], and Wood and Roth[6]) the role of the temperature T^* and of the duration t^* of the prerelaxation was left somewhat unclear. Also the question of the absolute value of the stress was not discussed.

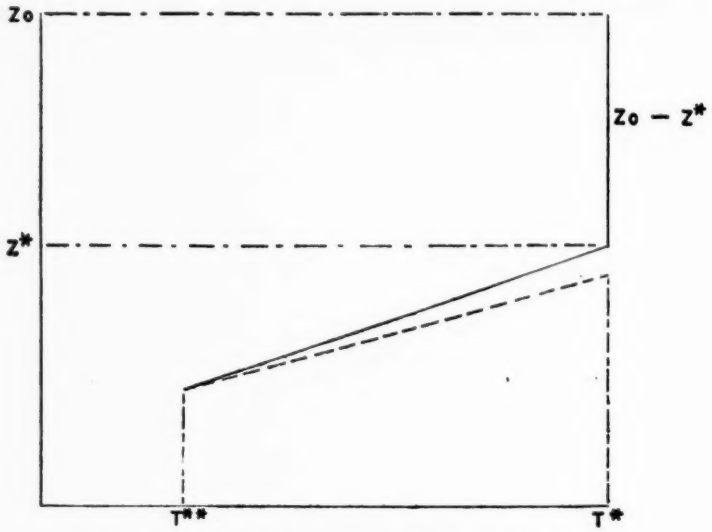


FIG. 4.—Isometric obtained after prerelaxation according to Figure 3.

STRESS RELAXATION

The importance of the prerelaxation in the relaxation method for isometrics necessitates a closer study of the laws of stress relaxation.

Our experimental work on the stress relaxation of natural and synthetic gum and tread stocks may be summarized in the factorization relation:

$$Z(\epsilon, T; t) = F(\epsilon, T), G(t, T) \tag{3}$$

Stress relaxation differs from the equation of state in the entering of the time as a new variable. This means, for instance, that it is not possible to derive from all times t the laws of creep (Z = const.) from Equation (3) by solving for ϵ.

The Equation (3) implies the constancy of the following ratios:

$$\frac{Z(\epsilon'', T; t)}{Z(\epsilon', T; t)} = \frac{Z(\epsilon'', T; t_2)}{Z(\epsilon', T; t_2)} = \cdots = \frac{F(\epsilon'', T)}{F(\epsilon', T)} \tag{4a}$$

$$\frac{Z(\epsilon_1, T; t'')}{Z(\epsilon_1, T; t')} = \frac{Z(\epsilon_2, T; t'')}{Z(\epsilon_2, T; t')} = \cdots = \frac{G(t'', T)}{G(t', T)} \tag{4b}$$

The meaning of the notation in Equations (4a) and (4b) is made clear in Figures 5*a* and 5*b*. These figures exhibit the geometric implications of the factorization. The relaxation ($Z - t$) curves for various constant extensions ϵ and the stress-strain ($Z - \epsilon$) curves[7] for various constant times t', t'', . . . are similar, *i.e.*, they may all be superposed on each other by multiplication by constant factors.

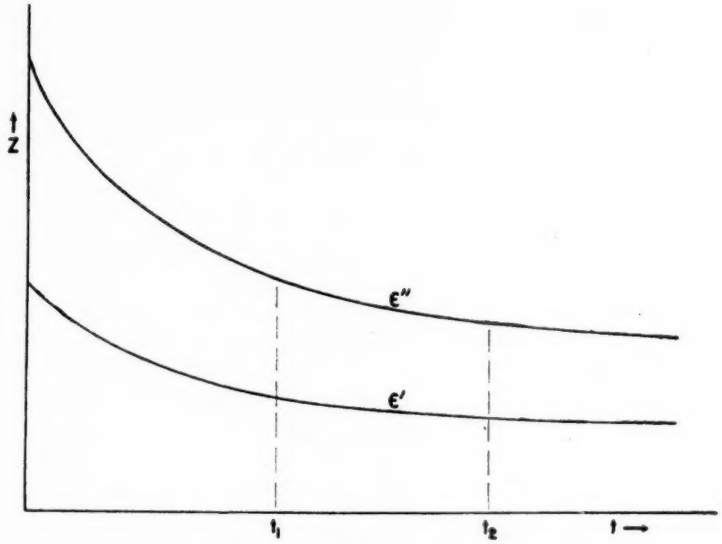


FIG. 5*a*.—Similarity of stress-time curves.

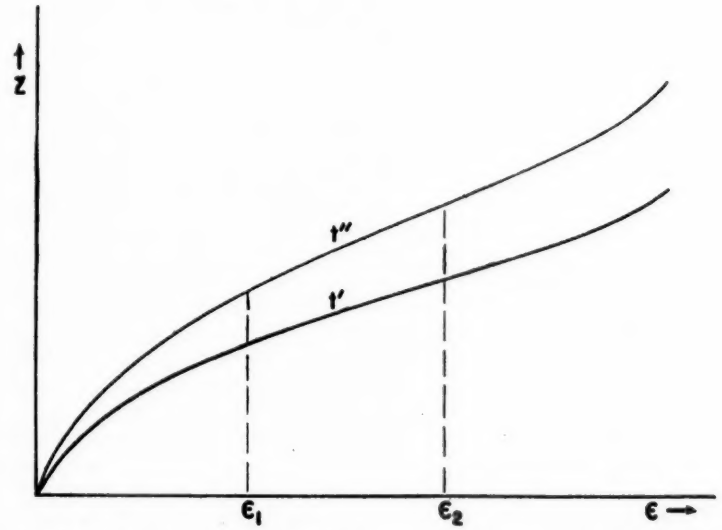


FIG. 5*b*.—Similarity of stress-strain curves obtained from stress-time curves of the type shown in Figure 5*a*.

GENERAL THEORY OF TIME ELASTICITY

Time elasticity shall designate any process in which stresses cause deformations with the time element as an important factor. A general formalism may be given in agreement with the factorization (Equation (3)) by a generalization of Boltzmann's theory of time-elastic processes.

The fundamental integral equation is:

$$Z(t) = F[\epsilon(t)] - \beta \int_{-\infty}^{t} \varphi(t - t')F[\epsilon(t')]dt' \tag{5}$$

β is a (small) constant. $\beta\varphi(t - t')$ is the memory function of Boltzmann. Equation (5) reduces to Boltzmann's equation, if the instantaneous stress-strain relation:

$$Z = F(\epsilon) \tag{6a}$$

reduces to Hooke's law:

$$Z = E\epsilon \tag{6b}$$

where the constant E denotes Young's modulus.

For relaxation:

$$\epsilon(t) = \epsilon(t') = \begin{cases} 0, & t < 0 \\ \epsilon = \text{const.}, & t > 0 \end{cases}$$

Equation (5) reduces to:

$$Z(t, \epsilon) = F(\epsilon)[1 - \beta\psi(t)] = F(\epsilon)G(t) \tag{7}$$

where:

$$\psi(t) = \int_{0}^{t} \varphi(t - t')dt \tag{8}$$

Equation (7) is identical with Equation (3). (For simplicity we did not indicate in Equation (5) the temperature as another variable.)

For creep we have to invert our fundamental Equation (5). For short times this is simple. Then the term with β will be small and terms of order β^2 or higher may be neglected. We obtain:

$$\epsilon(t) = F^{-1}\left\{Z(t) + \beta \int_{-\infty}^{t} \varphi(t - t')Z(t')dt'\right\} \tag{9}$$

and for creep:

$$Z(t) = Z(t') = \begin{cases} 0, & t < 0 \\ Z = \text{const.}, & t > 0 \end{cases}$$

$$\epsilon(t) = F^{-1}\{Z[1 + \beta\psi(t)]\} \tag{10}$$

Equation (10) follows from Equation (7) by solving for ϵ and yields factorization for creep in the special case of Hooke's law, where $\epsilon = F^{-1}(Z) = Z/E$ but not in the general case of Equation (6a). We notice that, had we assumed factorization for creep, we would have arrived at an equation different from (9) which would have contradicted Equation (5). Our experiments show that —in contrast to relaxation—factorization does not hold for creep.

All time-elastic phenomena may be derived from the fundamental Equation (5). For instance, we can obtain the dependence on time of stress-strain curves obtained at constant rate of loading or of stretching[8]. The fast processes of forced or free vibrations may be treated, using the same equation as a general frame.

The determination of the memory function from molecular models we shall defer to another paper. The function $Z = F(\epsilon)$ is the stress-strain relation as given by the statistical theory of rubber elasticity:[1]

$$Z = K \cdot T \left[1 + \epsilon - \frac{1}{(1+\epsilon)^2} \right]. \tag{11}$$

For shear deformations, Hooke's law (6b) holds (with ϵ as shear-strain) up to moderate extensions and Equation (5) reduces to Boltzmann's. For shear there is then factorization for both creep and relaxation.

THEORY OF ISOMETRICS FROM RELAXATION METHOD

Experimental work at Notre Dame on natural and synthetic gum stock may be summarized in the relation:

$$Z(\epsilon, T; T^*, t^*) = F(\epsilon, T), G(T^*, t^*) \tag{12}$$

Here T^* and t^* designate the temperature and duration of the prerelaxation process which precedes the taking of the isometrics (cf. Figures 3 and 4). Equation (12) expresses a generalized factorization. Again, as in the case of simple relaxation (to which Equation (12) refers for $T^* = T$), the constancy of certain ratios is implied in Equation (12):

$$\frac{Z(\epsilon'', T; T^*, t^*)}{Z(\epsilon', T; T^*, t^*)} = \frac{F(\epsilon'', T)}{F(\epsilon', T)} \tag{13a}$$

$$\frac{Z(\epsilon, T''; T^*, t^*)}{Z(\epsilon, T'; T^*, t^*)} = \frac{F(\epsilon, T'')}{F(\epsilon, T')} \tag{13b}$$

$$\frac{Z(\epsilon, T; T_2^*, t^*)}{Z(\epsilon, T; T_1^*, t^*)} = \frac{G(T_2^*, t^*)}{G(T_1^*, t^*)} \tag{13c}$$

$$\frac{Z(\epsilon, T; T^*, t_2^*)}{Z(\epsilon, T; T^*, t_1^*)} = \frac{G(T^*, t_2^*)}{G(T^*, t_1^*)} \tag{13d}$$

Again the constancy of these four ratios means geometrically the similarity of certain curves derived from the stress-temperature-time relationships.

The factorization expressed in Equation (12) shows clearly that all isometrics for various times t^* or temperatures T^* of prerelaxation differ only by a numerical factor $G(T^*, t^*)$. This factor is determined by the form of Boltzmann's memory function, as explained in Section 4. Equation (12) also shows that the initial unstretched length should be taken for the computation of the extension ϵ. Thus the functional form of the equation of state may be obtained unambiguously from experiment.

The question of the absolute value of the stress is connected with the particular form of the memory function, *i.e.*, with the statistical model used to explain the memory function.

Suppose the time elasticity of our material is given by a Maxwell body, *i.e.*, a spring and a dashpot in series, leading to permanent set. Then one should extrapolate the time factor G to $t = 0$. On the other hand, if the time elasticity is better described by a Maxwell body in parallel with a spring (leading to temporary set only), then one should extrapolate G to $t = \infty$. We restrict ourselves here to these two examples.

LIMITATIONS

The experimental results which yielded similarity for simple stress relaxation and for isometrics, using prerelaxation, were obtained in air in the temperature range of 0–70° C.

The interesting work of Tobolsky and his associates[9] at Princeton showed that relaxation and creep of rubber at temperatures above 100° C is caused by chemical changes involving the breaking and formation of primary valence bonds. The similarity law of Equation (3) is valid. For our temperature range of 0–70° C, however, these processes are less important. In fact, in our experiments there was comparatively little permanent set left after taking the isometrics.

We wish to point out that there is always an observable decay of stress during the relaxation. Figures (6) and (7) of Tobolsky and Andrews[10] are only in apparent contradiction to this statement. The apparent constancy of Z/T in these figures is caused by the small scale employed. Blown up to a larger scale, their results show also a stress decay.

Long duration creep and relaxation tests were carried out by Mooney, Wolstenholme, and Villars[11] at 35° and 70° C. For moderate extensions and duration their data are compatible with similarity.

It is planned to publish in greater detail in the near future the work summarized briefly in this paper. There, among other things, the role of the ordinary thermal expansion of rubber will be discussed.

RÉSUMÉ

The physical significance of stress-strain curves and of isometrics obtained by the relaxation method is discussed and clarified. Stress-strain curves taken at various temperatures give the correct dependence of stress on temperature if they are taken sufficiently fast so that stress relaxation does not mask the temperature dependence. Isometrics obtained after previous relaxation of the sample are shown to depend on duration and temperature of the relaxation by a numerical factor only. The basis for this behavior is the factorization of the stress into a factor depending on extension and temperature only which corresponds to the equation of state and another factor depending on the temperature T^* and the duration of the relaxation process. For simple stress relaxation, the same factorization holds with T^* equal to T. A general theory is formulated for time-dependent elastic phenomena by generalizing Boltzmann's theory. The theory explains why factorization does not hold for creep, in agreement with experiment.

REFERENCES

[1] James and Guth, *J. Chem. Phys.* **11**, 455 (1943).
[2] Dart, Anthony and Wack, *Rev. Sci. Instruments* **17**, 106 (1946).
[3] Because of the rise of temperature on fast stretching, these stress-strain curves are in reality adiabatics. However, the difference between adiabatics and isothermals is within the experimental error for extensions up to crystallization.
[4] Meyer and Ferri, *Helv. Chim. Acta* **18**, 570 (1935); RUBBER CHEM. TECH. **8**, 319 (1935).
[5] Anthony, Caston and Guth, *J. Phys. Chem.* **46**, 826 (1942); RUBBER CHEMISTRY TECH. **16**, 297 (1943).
[6] Wood and Roth, *J. Applied Physics* **15**, 781 (1944).
[7] These stress-strain curves are obtained by cross-plotting from the relaxation curves (Figure 5*a*). They differ from stress-strain curves obtained at a constant rate of loading or stretching.
[8] See Slominsky, *Acta Phys. Chem. U.S.S.R.* **12**, 99 (1940) for the case of Boltzmann's theory.
[9] Tobolsky and Andrews, *J. Chem. Phys.* **13**, 3 (1945).
[10] Tobolsky and Andrews, *J. Chem. Phys.* **13**, 9 (1945).
[11] Mooney, Wolstenholme and Villars, *J. Applied Phys.* **15**, 324 (1944).

CRYSTALLIZATION OF UNVULCANIZED RUBBER AT DIFFERENT TEMPERATURES *

LAWRENCE A. WOOD AND NORMAN BEKKEDAHL

NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.

I. INTRODUCTION

Crystals may be formed in natural rubber under varied experimental conditions. Different combinations of stretching and cooling have been used to induce crystallization in unvulcanized and in vulcanized rubber. The appearance and disappearance of crystals have been studied by observations of the volume[1], heat capacity[2], light absorption[3], birefringence[4], x-ray diffraction[5], hardness[3], and other mechanical properties[6]. There has, however, been no comprehensive study of the effect of temperature on the crystallization. The present investigation was undertaken to explore this field.

In the work reported here it has been the aim to study crystallization at different temperatures under the simplest possible conditions. The main features of the crystallization of vulcanized rubber have been shown[7] to be similar to those of the crystallization of unvulcanized rubber, vulcanization decreasing the rate of crystallization. Consequently unvulcanized rubber was selected for study. Stretching obviously complicates the experimental conditions, and so was not employed. Of the different methods of measuring crystallization, it seems that change of volume is the simplest and best adapted to yielding quantitative data on the course of the crystallization or fusion. The present work is, therefore, concerned with a general study of the volume changes in unvulcanized rubber at different temperatures.

II. EXPERIMENTAL PROCEDURE

The volume changes of the specimens were measured by the use of dilatometers with confining liquids. The technique incorporates some improvements over that previously used[1]. The dilatometers were made of Pyrex glass, and each consisted merely of a bulb with a capillary tube sealed to it. Changes in volume could be calculated from measurements of changes in the height of the confining liquid in the capillary tube. Mercury was selected as the confining liquid because it seems to have no effect on rubber, even when the two are in contact for periods of several years. Some absorption, swelling, and softening usually occur with other liquids. The specimens were strips cut from plantation smoked-sheet rubber.

The construction of the dilatometers and the procedure for filling them were somewhat improved during the course of the work reported here. In the later dilatometers the capillary tubes were about 2 mm. in inside diameter and about 500 mm. long. They were specially selected capillaries, but were not of the precision-bore type recently developed. They were graduated in millimeters along their length. The tubes were calibrated by sealing a stopcock

* Reprinted from the *Journal of Applied Physics*, Vol. 17, No. 5, pages 362–375, May 1946.

to one end, and observing the lengths of weighed amounts of mercury at five or more different points along each tube. The maximum variation in cross-sectional area along a single capillary was found to be about 3 per cent in most cases. Each capillary was then sealed to a glass tube of about 15 mm. inside diameter; the other end of the tube was left open. Into the glass tube were inserted a weighed rubber specimen and a hollow glass bulb about 40 or 50 mm. long. Finally the open end of the glass tube was sealed off to form the bulb of the dilatometer.

This construction made it possible to avoid heating the specimen during the sealing operation, without unduly increasing the net volume of the dilatometer bulb. In most cases the volume of the specimen was between two and three times the volume of the mercury in the bulb of the dilatometer. The effect of the insertion of the hollow bulb is equivalent to a mere reduction of the net volume of the dilatometer bulb. Since the inner hollow bulb was made of the same type of glass as the rest of the dilatometer, neither its volume nor its expansivity entered directly into any of the calculations.

The dilatometer was next evacuated for several days to remove gas from the specimen. Mercury was then admitted to the evacuated system, through a two-way stopcock, until it filled the dilatometer bulb and stood at a suitable height in the capillary. Occasionally it was necessary to carry out further removal of gas until the height of the mercury in the capillary did not change by more than a few millimeters as the pressure was again raised to that of the atmosphere. Calculation showed that the gas remaining under these conditions would have a negligible effect on the observed specific volume and expansivity. The dilatometer was weighed before and after the addition of the mercury.

The volumes of specimen and mercury at 25° C were determined from their weights and densities. The densities of the rubber specimens at this temperature were measured by the method of hydrostatic weightings. The volume of the dilatometer up to the level of the mercury in the capillary at this temperature was obtained as the sum of the volumes of the mercury and the specimen. At any other temperature the volume up to the same point on the capillary was found from the known expansivity of Pyrex glass. The volume of the dilatometer up to any other point on the capillary could then be calculated from the calibration of the capillary. The volume of the specimen corresponding to each observation was obtained by subtracting from this volume the volume of the mercury at the temperature of the observation.

After the specimens and dilatometers had been prepared, they were usually placed in a stirred bath of about 6 liters of alcohol cooled by solid carbon dioxide to a temperature of about −39° C, an approximate lower limit set by the freezing of the mercury. Observations of the height of the mercury in the capillary were made as the temperature was raised to +55° C at a rate of the order of 0.5° C per minute. At the lower temperatures the bath was warmed at about this rate by the heat from its surroundings. Beginning at about −10° C, additional heat was furnished by means of a knife-type immersion heater controlled by a Variac. The alcohol was usually replaced with water for measurements above room temperature. In this manner the volume-temperature relation of the amorphous rubber was obtained. This relation, which is linear over a considerable range of temperature, will be described and discussed in greater detail later in connection with the melting of crystalline rubber.

It was found in preliminary experiments that, at a heating rate of 0.5° C per minute or less, no observable differences from the equilibrium values of the volume could be noted. At a heating rate of about 1° C per minute, the ap-

parent volume lagged behind the equilibrium value by an amount equivalent to about 1° C. At a heating rate of about 2° per minute, the lag was about 2° C.

The dilatometers were next placed in a small unstirred alcohol bath in a refrigerator at the temperature at which it was desired to crystallize the rubber. Observations of the height of the liquid in the capillary tube were made periodically and usually continued until no further volume change could be noted.

When it was observed in this manner that the rate of crystallization had become inappreciable, the specimens were placed in the stirred bath of alcohol cooled by solid carbon dioxide to a temperature of about −39° C. Observations of the volume were made as before, as the temperature was raised, and the volume-temperature relation of the crystalline rubber was obtained.

In a number of cases, to be described in detail later, there were deviations from this standard procedure for the purpose of studying the effect of varying some of the experimental conditions, or because the importance of some of the exact conditions was not realized at the time the experiment was performed.

III. EXPERIMENTAL RESULTS

1. RATE OF CRYSTALLIZATION

When crystallization was carried out according to the procedure just described, it was found that the rate was very low at first, increased to a maximum, and decreased to a negligible value. The volume-time relation at constant temperature thus has the sigmoid shape which has previously been given[8] for crystallization near 0° C. Figure 1 shows two families of such curves, one for crystallizing temperatures of −22° C and above, the other for −22° C and below.

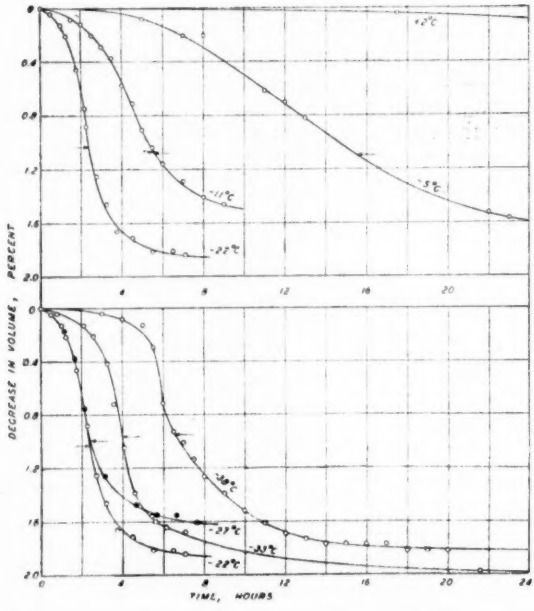


FIG. 1.—*Crystallization of rubber at different temperatures as indicated by decrease in volume.* The arrows indicate the estimated values for half the total decrease of volume at each temperature.

Since the volume is changing very slowly in the final stages, a determination of the time required for completion is somewhat uncertain. The time required for one-half the total change in volume is much more precisely determinable, since the curves are usually steepest near this point. The time required for half the volume change has been measured at a number of different temperatures. The reciprocal of this time, it can be readily seen, is a measure of the average rate of crystallization during the first half of the process. It is plotted as a function of temperature in Figure 2.

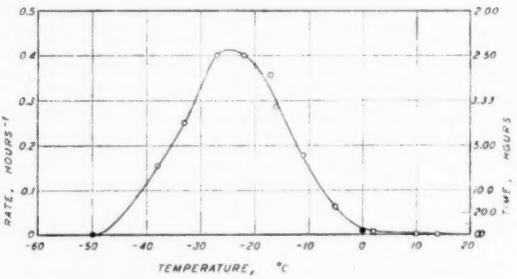


FIG. 2.—*Rate of crystallization of rubber.* The rate plotted is the reciprocal of the time required for one-half the total volume change.

2. THE MELTING OF CRYSTALLIZED RUBBER

When the volume-temperature relation of crystalline rubber is investigated, as already described, curves of the type shown in Figure 3 are obtained for increasing temperatures.

It can readily be seen that melting of the crystals occurs over a range of temperature, and that the range is markedly dependent on the temperature at which crystallization has occurred[9]. The temperature corresponding to the beginning of melting is that at which the volume begins to deviate from the curve representing the normal thermal expansion of crystalline rubber. Over the range of temperatures under consideration here the normal expansion curve is linear, and the temperature at which deviation begins to occur can be located within about one-half a degree. Similarly melting is complete when the volume

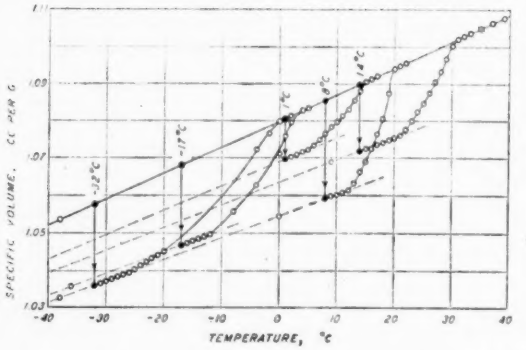


FIG. 3.—*Crystallization of rubber at different temperatures and subsequent melting.* The change of specific volume on crystallization is indicated by the vertical lines joining the dark circles.

again reaches the nearly linear curve which represents the volume-temperature relation of amorphous rubber and which was evaluated earlier.

There was found to be no evidence of any time lag or delay in melting of the crystals after the establishment of thermal equilibrium. For example, at any constant temperature in the melting range the volume was never observed to increase with time. In this range if the temperature is lowered, the volume-temperature relation is observed to be linear and intermediate between the amorphous and crystalline volumes. Rubber in the partially-melted state, however, can undergo additional crystallization with a resulting decrease of volume. If the temperature at which the additional crystallization occurs is the same as that at which the first crystallization has occurred, the melting curve is identical with that obtained from the complete melting of the first crystals. If the additional crystallization occurs at a different temperature from the first crystallization, two different ranges of melting will be observed, corresponding independently to the two temperatures of crystallization. Further discussion of this effect will be given below in the section on stark rubber, and is illustrated in Figure 7 in that section.

The additional crystallization possible in partially melted rubber, mentioned in the preceding paragraph, is considered in more detail in the section dealing with recrystallization. At this stage, however, it should be pointed out that the phenomenon may give rise to difficulty in determining the upper end of the melting range itself.

The rate of crystallization at certain temperatures was sufficiently great to make possible significant recrystallization during the time that the temperature was being raised through the melting range of the original crystals. Since recrystallization took place at a higher temperature than the original crystallization, the new crystals melted at a higher temperature than the original crystals, and the apparent upper end of the melting range was displaced upward by an amount which depended on the rate of temperature rise during melting.

When the initial crystallization occurred below 0° C, therefore, the upper end of the melting range was determined from a series of experiments at each temperature of crystallization. A stirred bath was adjusted to the approximate temperature of the upper end of the melting range. The dilatometer was then removed from the bath in which the original crystallization had been taking place and plunged into the stirred bath. The volume of the specimen increased because of both thermal expansion and the melting of the crystals. In less than five minutes, a reasonable time for the establishment of temperature equilibrium, the volume became constant. After an interval of time, the volume began to decrease because of recrystallization at the temperature of the stirred bath.

If the value of the volume when temperature equilibrium had become established and before observable recrystallization had occurred was the same as that originally observed for amorphous rubber at the corresponding temperature, it was concluded that the temperature of the stirred bath was at or above the upper end of the melting range. If the volume at equilibrium was less than that of the amorphous rubber at that temperature, the conclusion was drawn that melting was incomplete and that the temperature of the bath was below the upper end of the melting range. As might be expected, the volume at equilibrium was never found to be greater than the volume of the amorphous rubber. A series of experiments of this sort served to locate the upper end of the melting range which corresponded to a single temperature of original crystallization, and an additional series was required for each other temperature.

If the initial crystallization occurred at 0° C or above, the rate of recrystallization during melting was found to be so small as not to be significant during the time the specimen was in the melting range when the usual heating rates were employed. At these temperatures the range was of the order of 10° or less, and the time required to cover the range was usually between 20 and 30 minutes. The upper end of the melting range was determined from curves of the type shown in Figure 3 for all cases where the initial crystallization was at 0° C or above.

The results of a number of individual experiments of this sort are plotted in Figure 4, which shows the melting range as a function of the temperature of crystallization.

In one series of experiments a specimen was successively crystallized and melted sixteen times. After each melting the temperature was raised by different amounts varying from 1° to 40° above the end of the melting range. In all cases the same melting range was obtained on subsequent crystallization at a fixed temperature.

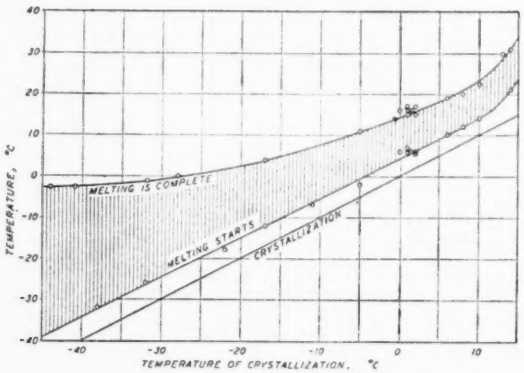


FIG. 4.—*Melting range of crystalline rubber as a function of the temperature of crystallization.* The lower line shows the crystallization temperature also as ordinate for easier comparison with the range of melting.

3. PARTIAL CRYSTALLIZATION

The melting range of partially crystallized rubber has been found to be the same as that obtained when crystallization is more nearly complete. Data regarding this point were obtained from a series of experiments in which the specimen was kept at 2° C for different lengths of time, and the melting range of the resulting crystals was then measured. In the first experiment after twenty days of crystallization the volume decrease amounted to 2.7 per cent. In the second experiment crystallization was interrupted at the end of nine days when the volume change amounted to only 1.0 per cent (or 37 per cent of the volume change in the first experiment). In the third experiment by interruption of the crystallization after one day, the volume change was limited to 0.085 per cent (or 3.1 per cent of that in the first experiment). The melting range in all three cases was 6° to 16° C within the accuracy of determination. On the basis of these experiments the crystallization in some cases was not carried completely to the point where the volume had ceased to change at a significant rate. Cases of this sort will be observed in Figure 3.

4. THE RECRYSTALLIZATION OF RUBBER

It will be noted that, in the cases previously described, the specimens were heated to at least 55° C immediately before crystallization. The purpose of this heating was to destroy centers of crystallization which might have been persisting from previous crystallizations, and which would have altered the rate of crystallization. A study of the rate of recrystallization when the specimen had not received such heating will now be described.

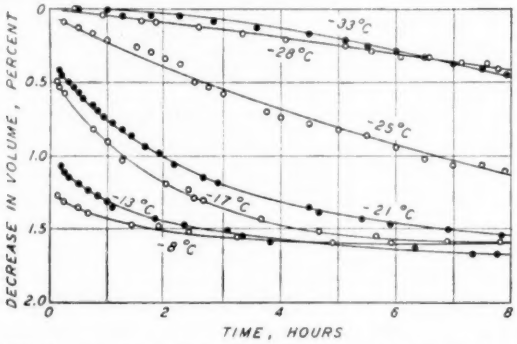


FIG. 5.—*Recrystallization of rubber at 0° C.* The curves show the change of volume as a function of time, after preliminary crystallizations at the fixed temperatures indicated on the curves. The zero on the ordinate axis represents the volume of amorphous rubber at 0° C. The zero on the time scale represents the time at which the dilatometer was plunged into the bath at 0° C. Observations taken in the first five minutes, before the attainment of temperature equilibrium, are omitted. The upper ends of the melting ranges as read from Figure 4, corresponding to the different temperatures of preliminary crystallization, are −2°, −1°, +1°, +2°, +4°, +6°, and +9° C, respectively.

The preliminary crystallization was first carried out overnight at −33° C according to the standard procedure already described. The specimen was then plunged into a bath held at 0° C and observations made of the change of volume with time. It will be noted from Figure 4 that the melting of crystals formed at −33° C is complete below 0° C. At first there was a volume increase due to thermal expansion and to the melting of the crystals. This

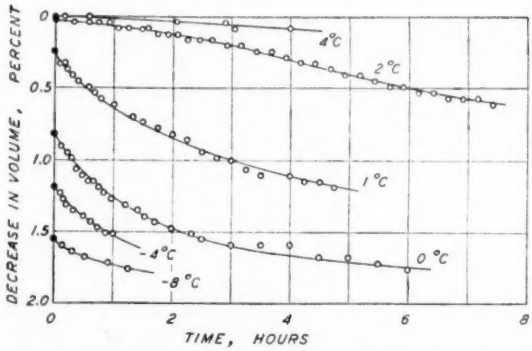


FIG. 6.—*Recrystallization of rubber after preliminary crystallization at −18° C.* The curves show the change of volume as a function of time at the temperatures indicated. The zero on the ordinate axis represents, in each case, the volume of amorphous rubber at these temperatures. The zero on the time scale represents the time at which the dilatometer was plunged into the bath at the temperatures indicated. The dark circles represent the volume observed immediately after the attainment of thermal equilibrium. The upper end of the melting range, as read from Figure 4, corresponding to preliminary crystallization at −18° C is +4° C.

change was found to be complete within about five minutes, a reasonable time for the establishment of thermal equilibrium. After an interval of time there was a volume decrease due to recrystallization at 0°. The whole procedure was repeated with the preliminary crystallization occurring at −28°, −25°, −21°, −17°, −13°, and −8° C, respectively. The results are reproduced in Figure 5.

Similar results were obtained when the conditions were altered so that the preliminary crystallization was carried out in each case at −18° C and recrystallization at temperatures of −8°, −4°, 0°, +1°, and +4° C, respectively. The results are shown in Figure 6. The significance of these results is discussed in a later section.

5. STARK RUBBER

When received in temperature climates, crude rubber is sometimes found to be crystallized[10] and to have a melting range above room temperature. For convenience in the present discussion, crystalline rubber having a melting range extending above 25° C will be called stark rubber in accordance with the suggestion of Pickles[11] and Whitby[12], since it is stiff and rather rigid at room

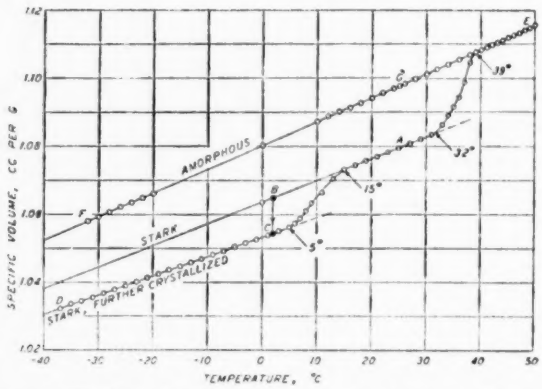


FIG. 7.—*Further crystallization and melting of a sample of stark rubber.* The specific volume of the sample as received is shown at *A*. It was cooled to *B*, where further crystallization occurred, reducing the specific volume to *C*. After cooling to *D* the temperature was raised to *E*. The temperature was lowered to *F* and then raised to room temperature at *G*.

temperature. The use of such a term is not intended to imply any essential fundamental difference between stark rubber and that melting at lower temperatures. It is to be presumed, on the basis of Figure 4, that, during the formation of the crystals in stark rubber, conditions were such that the stark rubber was crystallized at temperatures higher than about 10° C. No cases, other than those in the present paper, seem to have been reported in which the temperature of crystallization was measured (or even estimated, within 10° C) during the formation of stark rubber.

One sample of stark rubber, for which the authors are indebted to Professor H. I. Cramer, formerly of the University of Akron, was found to have a melting range from about 32° to 39° C. When specimens of this stark rubber were placed in a dilatometer and held at a temperature of about 1° C for forty-eight days, considerable additional crystallizaiion occurred, most of it within the first few days. When the specimens were melted in the usual manner, the curves shown in Figure 7 were obtained. The line between 16° and 32° C

passes through the points obtained before the stark rubber was held at 1° C for the additional crystallization.

In another experiment one end of a strip of stark rubber was immersed in water at 50° C for a few minutes. The lower end was thereby melted, while the upper end remained in the stark condition. When the whole strip was placed in a refrigerator at 1° C for several weeks, the lower end crystallized and could not be distinguished by visual or tactual observation from the upper end. However, when the strip was allowed to come to room temperature, the crystals in the lower end melted, as would be expected from Figure 4, while the upper end remained stark.

IV. DISCUSSION OF RESULTS

1. THE RATE OF CRYSTALLIZATION

It should be recognized that the measurements reported here regarding the rate of crystallization were all made on not more than two or three specimens of smoked sheet which had been heated to 55° C immediately before crystallization. The conditions of preparation of the rubber from the latex undoubtedly have a considerable influence on the rate of crystallization[6]. Uncoagulated latex itself showed no volume change when kept in a dilatometer at 2° C over a period of several months. This behavior confirmed previous observations in this laboratory[13]. Likewise, qualitative observation showed that crystallization was extremely slow in a sheet of evaporated latex. In this case crystallization appeared to take place most readily in certain regions. This effect is similar to the "patchy crystallization" described by Treloar[14], who reported that visual observations on a sample of smoked sheet showed that neighboring portions crystallized at widely different rates. No attempt was made in the present work to investigate the exact reasons for such differences. Various factors which have been reported to increase the rate of crystallization are residual stresses remaining after previous mechanical treatment, moderate pressure[15] and exposure to a beam of x-rays[16]. Very high pressures may inhibit crystallization[17]. The effect of previous thermal treatment on the rate of crystallization is discussed in the sections dealing with recrystallization.

It would appear reasonable from theoretical considerations to suppose that an increase of mobility of the atomic chains, brought about, for example, by mastication of the rubber, would increase the rate of crystallization. Although Van Rossem and Lotichius[3] could find only insignificant differences in the rate of crystallization with increasing times of milling, Katz[18], Gehman[5], and Cotton[19] all state that masticated rubber crystallizes more readily than unmasticated. The reverse effect, a decrease in the rate of crystallization caused by a decrease in the mobility of the chains on vulcanization, has already been described[7].

The rates of crystallization observed in the present work are in reasonable agreement with observations of density by Bekkedahl[13] and Treloar[14] at 0° C, by Smith and Hanna[20] at −20° C, and by Van Rossem and Lotichius[3] at 4° C and −10° C. Likewise a similar rate can be calculated from observations of Young's modulus at 0° C made by Conant and Liska[21].

2. LOWER LIMIT OF TEMPERATURE OF CRYSTALLIZATION

It has been recognized for some years that rubber does not crystallize at extremely low temperatures. No crystallization was evident in a specimen[13] cooled at −259° C, or in another[22] held at −190° C for 8 days. Other speci-

mens[23] were kept between −50° C and −78° C for 3 weeks without the occurrence of crystallization but did crystallize at −35° C and above. The present work serves to locate more definitely the lower limit of temperature at which crystallization is possible as about −50° C. Figure 2 shows that the rate of crystallization has become negligible below this temperature. Here the mobility is presumably insufficient to permit the orientation necessary for the formation of crystals. The supercooling of rubber is similar in this respect to that of selenium[24], sulfur, and many organic liquids.

3. UPPER LIMIT OF TEMPERATURE OF CRYSTALLIZATION

Crystallization has not been reported at the room temperatures (usually above 20° C) normally maintained in American laboratories. No evidence of it was noted in the present investigation when dilatometers were kept at room temperature over a period of a year or more. In European laboratories, however, where the temperatures are frequently near 15° C, the crystallization of rubber on storage has been noted on a number of occasions[25]. Cotton[19], for example, states: "When smoked sheet and crepe rubber have been in storage for some time, they gradually harden and assume a frozen condition. This is due to crystallization". In the present work the highest temperature at which crystallization was observed was 14° C. At this temperature, under the experimental conditions described here, the time required for crystallization is of the order of years. Crystallization at this temperature was continuing at an approximately constant rate when the experiment was discontinued after 289 days.

The crystallization observed in European laboratories appears to occur at a more rapid rate than this. Quite probably temperatures lower than 15° C during the night initiated the crystallization and the crystals then formed were not melted near 15° C during the day.

It is possible to increase the rate of crystallization by varying the previous thermal or mechanical treatment of the specimen, and thereby forming more centers of crystallization. Consequently, it is likely that the upper limit of temperature of crystallization shown in Figure 2 may be raised somewhat by the proper previous treatment of the rubber.

4. TEMPERATURE AT WHICH CRYSTALLIZATION IS MOST RAPID

The rate of crystallization was found to be a maximum at a temperature near −25° C, as can be seen in Figure 2. In the production of the form of raw rubber known as "cut sheet" or "patent rubber"[26], developed in Europe many years ago, rubber is crystallized so that it can be cut into sheets. The rubber is often held at a temperature of about −5° for a few days to bring about the crystallization. More recent books[27] state that the rubber should be held between −5° and −10° C for at least six days. No quantitative study of the rates at different temperatures, as in the present work, seems to have been reported previously.

5. MAGNITUDE OF THE VOLUME CHANGE ON CRYSTALLIZATION

The magnitude of the percentage decrease of volume on crystallization can be noted from curves of the type shown in Figure 1. The actual specific volume of the amorphous rubber varies with temperature, and can be read from curves like those in Figure 3. The decrease of specific volume on crystallization is,

of course, found to be the same as the increase of specific volume on subsequent melting. However, it might be pointed out that the percentage decrease of volume is not quite the same as the subsequent percentage increase of volume, since they are fractions of different quantities. Furthermore, any comparisons must be made at the same temperature.

In the present work in most cases the decreases of volume on crystallization were found to lie between 2.0 and 2.7 per cent. Repeated crystallizations of the same specimen under conditions which were thought to be identical did not always lead to the same volume changes. It seems possible that such variations are statistical fluctuations occasioned by the growth of crystals from different centers in different cases. There was an even greater variation in the decreases of volume when different specimens were studied, but in almost all cases the values lay within the limits given. The exact value, within these limits, seems to depend on factors which were not under control.

Values for this quantity, calculated from measurements of density or specific gravity reported by previous workers[28] generally lie within the same limits, although a few are somewhat lower. Holt and McPherson[29] found a volume change of about 1.85 per cent on stretching a specimen of vulcanized rubber to an elongation of 700 per cent at 25° C. Treloar[14], by stretching unvulcanized rubber at 0° C, observed a volume decrease of over 3 per cent, the highest value reported. With unstretched pale crepe he found a volume decrease of 2.3 per cent on crystallization at 0° C.

Observations made in the course of the present work furnish no data from which conclusions may be drawn as to the relative amounts of crystalline and amorphous material in a specimen.

Field [30] has recently conducted x-ray studies of this proportion of crystalline and amorphous components in stretched rubber, and concludes that, under favorable conditions, about 80 per cent of the material is in the crystalline state, in agreement with an earlier study by Meyer and Mark[31]. This value is considerably higher than those estimated by Parks[32] and Wildschut[33] by other methods. If reliance is to be placed on x-ray values, it would be very desirable to conduct several parallel studies of crystallization by means of x-rays and by means of observations of volume change. In this manner the relation between the percentage decrease of volume and percentage of crystalline material could be established.

6. MELTING OF CRYSTALLIZED RUBBER

The melting of the crystalline rubber is very much dependent on the temperature at which the crystals have been formed, as can be seen from Figures 3 and 4. This conclusion seemed so surprising that it was made the subject of a preliminary communication[9] based on only a part of the data reported in the present paper.

It can be seen that, the higher the temperature of crystallization, the higher are the temperatures at which both the beginning and ending of the melting occur. The beginning of melting occurs at a temperature of from 4° to 7° above that at which the crystals have been formed. For all temperatures of crystallization below about −35° C, the temperature at which melting is complete is about −2° C.

The range of melting becomes narrower the higher the temperature of crystallization up to about 0° C; for crystals formed at temperatures between 0° and 14° C, the range of melting is about 10°; for crystallization at higher

TABLE I

MELTING TEMPERATURES OF CRYSTALLINE RUBBER PREVIOUSLY REPORTED

Melting			Crystallization temperature (°C)	Observers	Technique	Remarks
Lower limit (°C)	Maximum change (°C)	Upper limit (°C)				
	43.5			Whitby[12]	Density	
	43			Whitby[12]	Density	
	41			Whitby[12]	Density	
	41			Barnes[34]	Visual	Flexibility Transparency
40				Wood, Bekkedahl, and Peters[35]	Linear expansion	
40		50	5 to 15	Feuchter[36]	Density	After 1 year
	up to 37			Katz[37]	x-Ray	
	36			Katz[38]	x-Ray	"old rubber"
	37			van Rossem and Lotichius[3]	Density, hardness, and light absorption	
35		45		Meyer, von Susich, and Valko[39]	x-Ray	
35				Wood, Bekkedahl, and Peters[35]	Linear expansion	
34	36	>40		van Rossem and Lotichius[3]	Density	Stored 13 years
	35			Feuchter and Hauser[40]	Retraction	1 year after racking
		35 to 40		von Susich[11]	x-Ray	
31.5		33		Cotton[19]		"Normally frozen"
30		40		Feuchter[36]	Density	Masticated
30		39		Katz[37]	Density	
30	33	35		Pickles (van Rossem)[11]	Density	
28	32	35		van Rossem and Lotichius[3]	Density	
27		29		Katz[37]	x-Ray	"Cut sheet"
25		36		Feuchter and Hauser[40]	Retraction	Racked
20		30		Katz[37]	x-Ray	
20		30		Bunschoten[12]	Density	

TABLE I.—*Continued*

Bunschoten[42] — Density

TABLE 1.—*Continued*

Melting: Lower limit (°C)	Melting: Maximum change (°C)	Melting: Upper limit (°C)	Crystallization temperature (°C)	Observers	Technique	Remarks
20	25	30	Cool cellar	Ruhemann and Simon[43]	Specific heat	Smoked sheet
		<30	−5.8	Carson[44]		
20		24		Hock[45]	Retraction	
20		23		Hock[46]	Retraction	
20		23	7 to 10	Thiessen and Kirsch[47]	x-Ray	Crystallized under pressure of 10–25 atmospheres
10	18	30	−15	Ruhemann and Simon[43]	Specific heat	"Cut sheets" crystallized at 150 atmospheres
11		13	6	Thiessen and Kirsch[48]	x-Ray	Pressure of 30 atmospheres
9.5		11	−58 to −43	Smith, Saylor and Wing[49]	Birefringence	Sol rubber crystallized from solution
8		10		Cotton[19]	Visual	Frozen in refrigerator
		<20	0 to 2	Katz and Bing[50]	x-Ray	
		<20	−5 to −10	Katz[51]	x-Ray	
		<20	−10	Katz and Bing[50]	x-Ray	
6	11	17	2	Bekkedahl and Wood[7]	Volume	Vulcanized rubber
6	11	16	0	Bekkedahl[13]	Volume	
	10			Park[52]	—	
2		14	−10	van Rossem and Lotichius[3]	Density and hardness	
0	5	10		Ruhemann and Simon[43]	Specific heat	
−2		14	−50	Smith and Saylor[53]	Birefringence	Gel crystallized from solution
−5.5		16	−25	Smith and Saylor[54]	Birefringence	
−15	11	17	<0	Bekkedahl and Matheson[2]	Specific heat	
	0			Bunn and Garner[55]	—	
−20		10		Ruhemann and Simon[43]	Specific heat	Beta-anomaly

temperatures no direct observations are available, but the range is probably narrower, since it appears that stark rubber has a somewhat narrower range of melting the higher the mean temperature of the range.

The results presented here undoubtedly explain many previously reported discrepancies in the temperatures of melting of crystalline rubber. Unfortunately in only a few cases have previous workers specified the temperature at which crystallization occurred. The variations in the melting have sometimes been thought to be connected with the variety of rubber, or the experimental technique. In most cases no explanation at all was attempted. Table I presents the results of measurements of the melting temperatures of crystalline rubber, as reported by previous observers. In those instances in which temperature of crystallization was reported, the only pronounced deviations from the results of Figure 4 are in the few instances where the crystals were formed from solution rather than from the bulk material.

A study of the table confirms the conclusion of the present investigation that there are not merely two forms of crystalline rubber, as has sometimes been suggested[56], but rather that crystals melting at any temperature between about $-40°$ and $+45°$ C may be formed in rubber by the proper choice of temperature for crystallization. It is rather surprising that such a conclusion has not been already drawn on the basis of the experimental data shown in Table I. The assignment of a definite melting point or melting range to rubber in general is thus seen to be without meaning in spite of the many investigators who have hoped to do so[57]. A recent writer[58] on the subject expresses considerable wonder at the variability of the melting point.

The temperature at which retraction of stretched rubber occurs is sometimes associated with the melting of crystals formed on stretching. Although the scope of the present investigation did not include any measurements on stretched rubber, some of the results may probably be safely applied to crystals formed by stretching. For example the influence of the temperature of crystallization on melting seems to furnish an explanation of certain effects observed by Treloar[59] in the retraction of stretched rubber. He found that the recovery temperature depended on the temperature at which stretching was performed. Lacking the results reported here, he said "One would not expect the melting point of the crystals to depend on the temperature at which they were formed".

Some years ago Van Rossem and Lotichius[3] made a careful study of the crystallization of raw rubber. In the main, there seems to be no disagreement between their experimental results and those contained in the present paper. In one instance it now seems desirable to give to their results an interpretation different from the one originally given.

This instance, which is one of the best known of the conclusions of Van Rossem and Lotichius[3], is a statement that the melting temperature of one sample of stark rubber was 31°–33° C in 1919 and had become 35°–37° C in 1927. An examination of the graph giving the specific gravity values which are the basis for discussion shows that the terms "melting temperature" or "melting point" were limited to the steepest portions of the curves. The full melting range of the specimen observed in 1919 appears to extend from 28° to 35° C. The observations made in 1927 show that the melting range began at 34° and extended above 40° C, the highest temperature at which observations were made. Since the specimen measured in 1927 was not completely melted at 40°, its specific gravity did not come down to the value characteristic of the amorphous rubber, as did that of the specimen measured in 1919, where melting was apparently complete at 35° C. No indications were given regarding the

temperature at which the specimen was stored from 1919 to 1927. The observed change of melting range could be explained on the reasonable assumption that the temperature, at least part of the time, was between 28° and 34° C. Crystals melting below 34° would then be melted, and recrystallization at those temperatures would yield new crystals having a higher melting range, as already described in the section on recrystallization.

Thus there seems to be no assurance that Van Rossem and Lotichius would have found a rise in the melting range during storage at a constant temperature below 28° C. No such rise was observed in the course of the present work. The actual phenomena observed by Van Rossem and Lotichius can then be explained in terms of the results of the present paper, without recourse to speculative assumptions of changes in crystal size or polymerization.

The considerations developed in the present work on the melting of crystalline rubber have already been applied[60] to explain results obtained by Ruhemann and Simon[43] in measurements of specific heat. It has been pointed out that the beta-anomaly which they observed can be explained as a phenomenon of crystallization under the particular conditions of their experiments, without the assumption of an anomaly characteristic of rubber in general. The volume-temperature graphs which they give for rising temperatures are of the same form as those obtained in the present work when the rate of temperature rise was slow enough to permit recrystallization and subsequent melting at higher temperatures.

7. RECRYSTALLIZATION

A number of interesting conclusions may be drawn from the experiments on recrystallization illustrated in Figures 5 and 6. In the first place the rate of crystallization at a given temperature is much greater than in the instances previously discussed, where the standard procedure called for heating to at least 55° C before each crystallization to destroy possible centers of crystallization. An examination of Figure 1 shows that at 2° C after such treatment the change of volume in the first 10 hours is about 0.05 per cent. On the scales used in Figures 5 and 6, such a change would hardly be perceptible, and the experimental points would lie on an almost horizontal line through the origin. In the second place the effects of the preliminary crystallization in increasing the rate of subsequent crystallization extend at least several degrees above the upper end of the melting range. For example it is clear from Figure 6 that the melting range does not extend above 4° C, since the initial ordinate is zero for the recrystallization at 4° C. The rate of recrystallization at 4° C is seen to be of appreciable magnitude in comparison with the much lower rate which is observed when the centers of crystallization are destroyed by previous heating to 55° C.

The selection of a temperature of 55° C as being sufficient to destroy centers of crystallization was based on the fact that it was five or ten degrees above the highest temperature at which any crystals have been reported in unstretched rubber, as noted in Table I. In numerous experiments no evidence of any effect of previous thermal history was found to persist in any sample after heating it to 55° C.

Attention should be called to the two different types of crystallization curves shown in Figures 5 and 6. At temperatures below the upper end of the melting range, the rate of crystallization has its largest value at the beginning and decreases with increasing time. At temperatures above the upper end of the melting range, the rate of crystallization is small at the beginning, in-

creases with time to a maximum and, when observations are carried out over a sufficiently long period, decreases again to a negligible value. The latter curves are thus of the sigmoid type shown in Figure 1. One can therefore conclude from Figure 5 alone that the end of the melting range would be at 0° C, following crystallization at a temperature between −25° and −28° C. From Figure 4 this temperature is read as −28° C.

In terms of the usual conceptions of crystal growth it is possible to give a simple explanation of the difference between the two types of curves. In accordance with the ideas of Tammann and others[61], a crystal can be initiated only at certain centers or nuclei. The crystal, once initiated, grows from the center at a characteristic rate, called the linear crystallization velocity, until the available crystallizable material between it and the next crystal is exhausted.

In the first instance where crystallization represents merely further growth of crystals already present, no additional centers of crystallization are necessary. The rate of crystallization as measured by volume change is, therefore, a maximum at the beginning and decreases because of exhaustion of crystallizable material. In the second instance crystallization at the beginning is slow because of the lack of a sufficient number of centers from which crystals may grow. Crystals start from the available centers, and more centers are formed as time goes on[62]. Thus the rate of crystallization increases at first, reaches a maximum, and then decreases again with the exhaustion of crystallizable material.

At temperatures immediately above the upper end of the melting range there remains, of course, no crystalline material. However, centers of crystallization must persist at least several degrees above the end of the melting range, since the rate of recrystallization at these temperatures, as shown in Figure 7, is much greater than is the case when the centers of crystallization are destroyed by heating to 55° C.

8. NATURE OF THE CRYSTALS

The nature of the crystalline regions in long chain high polymers has been the subject of considerable discussion in recent years. Alfrey and Mark[63], Bunn[64], Treloar[65], and Wood[66] have summarized some of the ideas. It seems generally agreed, for instance, that the structural units of the crystallites are not whole molecules but rather kinetic units which are segments of chains. Consequently, a single chain may contain segments which are units in two or more different crystallites, joined by segments which are to be regarded as part of the amorphous material.

The scope of the present paper does not include any attempt to extend the detailed concept of the nature of the crystals on the basis of the results obtained here. It has already been pointed out elsewhere[66] that these results cast grave doubts on the acceptability of several theories proposed to account for the existence of a range of melting. The field is still open for a theory which will logically and satisfactorily explain two experimental observations reported here: (1) that the range of melting does not depend on the extent of crystallization, and (2) that it is definitely determined by the temperature at which crystallization occurs.

Crystals of a lower-melting type can be formed and melted in a specimen already containing crystals of a higher-melting type, as shown in the experiments illustrated by Figure 7. It is remarkable that the presence of crystals of the higher-melting type appears to have so little effect on the formation and melting of the lower-melting crystals. It does appear that the two types must

compete for crystallizable material, since the total volume change does not exceed 3 per cent in any case.

It cannot be emphasized too strongly that the sole important factor in determining the melting range is the temperature at which crystallization occurs. Other conditions may alter the rate of crystallization by a large factor or the volume change during crystallization, as already discussed, but the melting range remains the same. Even different degrees of vulcanization[7] do not alter the relation between melting range and temperature of crystallization. Thus, the quantitative results depicted in Figure 4 are regarded to be of much more general application than the other portions of the present investigation.

The experimental work described in this paper was performed between 1940 and 1942, but war activities prevented earlier publication, except for a preliminary note[9] on the change of melting range with temperature of crystallization.

RESUMÉ

The crystallization and melting of unvulcanized natural rubber in the unstretched state were investigated at different temperatures. Change of volume was used as a quantitative measure of the extent of crystallization, and mercury-filled dilatometers containing the rubber were used for the volume measurements. Crystallization was observed to occur at temperatures between $-50°$ and $+15°$ C and to be most rapid at about $-25°$ C. The final decrease of volume on crystallization was usually found to lie between 2.0 and 2.7 per cent. The melting of crystalline rubber was found to occur over a range of temperature and to be strongly dependent on the temperature at which the crystals were formed. The temperature at which the beginning of melting occurs is from 4° to 7° above the temperature of crystallization. The range of melting is about 35° at the lowest temperatures and decreases to about 10° at the highest. The same range of temperature of melting is obtained regardless of the extent of the crystallization.

REFERENCES

[1] Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934); RUBBER CHEM. TECH. **8**, 5 (1935); Bekkedah and Matheson, *J. Research Natl. Bur. Standards* **15**, 503 (1935); RUBBER CHEM. TECH. **9**, 264 (1936); Bekkedahl and Wood, *J. Chem. Phys.* **9**, 193 (1941); RUBBER CHEM. TECH. **14**, 544 (1941); *Ind. Eng. Chem.* **33**, 381 (1941); RUBBER CHEM. TECH. **14**, 347 (1941).

[2] Bekkedahl and Matheson, *J. Research Natl. Bur. Standards* **15**, 503 (1935); RUBBER CHEM. TECH. **9**, 264 (1936).

[3] Van Rossem and Lotichius, *Kautschuk* **5**, 2 (1929); RUBBER CHEM. TECH. **2**, 378 (1929).

[4] Thibodeau and McPherson, *J. Research Natl. Bur. Standards* **13**, 887 (1934); RUBBER CHEM. TECH. **8**, 183 (1935); Kirsch, "Equilibria between crystals and melts in rubber and their dependency on temperature and pressure", Thesis, Trillsch and Huther, Berlin, 1937; Smith and Saylor, *J. Research Natl. Bur. Standards* **21**, 257 (1938); RUBBER CHEM. TECH. **12**, 18 (1939); Thiessen and Wittstadt, *Z. physik. Chem.* **B41**, 33 (1938); RUBBER CHEM. TECH. **12**, 736 (1939); Wittstadt, *Kautschuk* **15**, 11 (1939); RUBBER CHEM. TECH. **12**, 488 (1939).

[5] Gehman, *Chem. Rev.* **26**, 203 (1940).

[6] Messenger and Scott, *J. Research Assocn. Brit. Rubber Manufrs.* **5**, 64 (1936); RUBBER CHEM. TECH. **10**, 7 (1937).

[7] Bekkedahl and Wood, *Ind. Eng. Chem.* **33**, 381 (1941); RUBBER CHEM. TECH. **14**, 347 (1941).

[8] Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934); RUBBER CHEM. TECH. **8**, 5 (1935); Bekkedahl and Wood, *Ind. Eng. Chem.* **33**, 381 (1941); RUBBER CHEM. TECH. **14**, 347 (1941); Treloar, *Trans. Faraday Soc.* **37**, 84 (1941); RUBBER CHEM. TECH. **15**, 251 (1942).

[9] Bekkedahl and Wood, *J. Chem. Phys.* **9**, 193 (1941); RUBBER CHEM. TECH. **14**, 544 (1941).

[10] Hauser and Rosbaud, *Kautschuk* **3**, 17 (1927); Hauser, Hünemörder and Rosbaud, *Kautschuk* **3**, 2281 (1927).

[11] Pickles, *India-Rubber J.* **67**, 69 (1924).

[12] Whitby, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, Reinhold Publishing Corp., New York, 1937, p. 102.

[13] Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934); RUBBER CHEM. TECH. **8**, 5 (1935).

[14] Treloar, *Trans. Faraday Soc.* **37**, 84 (1941); RUBBER CHEM. TECH. 15, 251 (1942).

[15] Kirsch, "Equilibria between crystals and melts in rubber and their dependency on temperature and pressure", Thesis, Trillsch and Huther, Berlin, 1937; Thiessen and Kirsch, *Naturwissenschaften* **27**, 387 (1938); RUBBER CHEM. TECH. **12**, 12 (1939); *Naturwissenschaften* **27**, 390 (1939); RUBBER CHEM. TECH. **13**, 48 (1940); Wood, Bekkedahl and Gibson, *J. Chem. Phys.* **13**, 475 (1945); *J. Research Natl. Bur. Standards* **35**, 375 (1945).

[16] Ott *J. Am. Chem. Soc.* **52**, 4612 (1930); RUBBER CHEM. TECH. 4, 82 (1931).

[17] Dow, *J. Chem. Phys.* **7**, 201 (1939); RUBBER CHEM. TECH. **12**, 496 (1939).
[18] Katz, *Gummi-Ztg.* **41**, 1 (1927).
[19] Cotton, *Trans. Inst. Rubber Ind.* **16**, 303 (1941); RUBBER CHEM. TECH. **14**, 762 (1941).
[20] Smith and Hanna, *J. Research Natl. Bur. Standards* **27**, 229 (1941); RUBBER CHEM. TECH. **15**, 265 (1942).
[21] Conant and Liska, *J. Applied Physics* **15**, 767 (1944); RUBBER CHEM. TECH. **18**, 318 (1945).
[22] Pummerer and Von Susich, *Kautschuk* **7**, 117 (1931); RUBBER CHEM. TECH. **5**, 245 (1932).
[23] Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934); RUBBER CHEM. TECH. **8**, 5 (1935); Park, *Mem. Coll. Sci. Kyoto Imp. Univ.* **A22**, 259 (1939); RUBBER CHEM. TECH. **13**, 539 (1940).
[24] Mondain-Monval, *Ann. chim.* **3**, 5 (1935).
[25] Katz and Bing, *Z. angew. Chem.* **38**, 439 (1925); Ott, *Naturwissenschaften* **14**, 320 (1926); Pummerer and von Susich, *Kautschuk* **7**, 117 (1931); RUBBER CHEM. TECH. **5**, 245 (1932); Meyer, von Susich and Valko, *Kolloid-Z.* **59**, 208 (1932).
[26] Gottlob, "Technology of Rubber", English translation by Rosenbaum, Maclaren Sons, Ltd., London, **1927**, p. 319.
[27] Thiele and Wurm, in Hauser, "Handbuch der Gesamten Kautschuktechnologie", Union Deutsche Verlagsgesellschaft, Berlin, **1935**, Vol. 2; Boström, Lange, Schmidt, and Stöcklin, "Kautschuk und verwandte Stoffe", Union Deutsche Verlagsgesellschaft, Berlin, **1940**; Roth & Co., Berlin, **1940**.
[28] Bunschoten, *Mededeel. Rijksvoorlichtingsdienst Behoeve Rubberhandel Rubbernijverheid*, Delft, No. 3, 37 (1921); Hock, *Z Elecktrochem.* **31**, 404 (1925); Feuchter, *Kautschuk* **2** 260, 282 (1926); Kirchhof, *Kautschuk* **2**, 151 (1926); Van Rossem and Lotichius, *Kautschuk* **5**, 2 (1929); RUBBER CHEM. TECH. **2**, 378 (1929); Sachse, *Gummi-Ztg.* **43**, 2216 (1929); Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934); RUBBER CHEM. TECH. **8**, 5 (1935); Whitby, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, Reinhold Publishing Corp., New York, **1937**, p. 102; Barnes, *Can. J. Research* **15**, 156 (1937); RUBBER CHEM. TECH **10**, 462 (1937); Bekkedahl and Wood, *Ind. Eng. Chem.* **33**, 381 (1941); RUBBER CHEM. TECH. **14**, 347 (1941); Smith and Hanna, *J. Research Natl. Bur. Standards* **27**, 229 (1941); RUBBER CHEM. TECH. **15**, 265 (1942).
[29] Holt and McPherson, *J. Research Natl. Bur. Standards* **17**, 657 (1936); RUBBER CHEM. TECH. **10**, 412 (1937).
[30] Field, *J. Applied Physics* **12**, 23 (1941); RUBBER CHEM. TECH. **14**, 555 (1941); Gehman and Field, *J. Applied Physics* **15**, 371 (1944); RUBBER CHEM. TECH. **17**, 640 (1944).
[31] Meyer and Mark, *Ber.* **61**, 1939 (1928).
[32] Parks, *J. Chem. Physics* **4**, 459 (1936); RUBBER CHEM. TECH. **10**, 135 (1937).
[33] Wildschut, *J. Applied Physics* **17**, 51 (1946).
[34] Barnes, *Can. J. Research* **15**, 156 (1937); RUBBER CHEM. TECH. **10**, 462 (1937).
[35] Wood, Bekkedahl and Peters, *J. Research Natl. Bur. Standards* **23**, 571 (1939); RUBBER CHEM. TECH. 13, 290 (1940).
[36] Feuchter, *Kautschuk* **2**, 260, 282 (1926).
[37] Katz, *Kautschuk* **5**, 6 (1929).
[38] Katz, *Trans. Faraday Soc.* **32**, 77 (1936); RUBBER CHEM. TECH. **9**, 357 (1936).
[39] Meyer, von Susich and Valko, *Kolloid-Z.* **59**, 208 (1932).
[40] Feuchter and Hauser, *Kautschuk* **5**, 194, 218, 245, 276 (1929).
[41] Von Susich, *Naturwissenschaften* **18**, 915 (1930); RUBBER CHEM. **4**, 211 (1931).
[42] Bunschoten, *Mededeel. Rijksvoorlichtingsdienst Behoeve Rubberhandel Rubbernijverheid*, Delft, No. 3, 37 (1921).
[43] Ruhemann and Simon, *Z. physik. Chem.* **A138**, 1 (1928).
[44] Carson, *Ind. Eng. Chem.* **23**, 691 (1931); RUBBER CHEM. TECH. **4**, 417 (1931).
[45] Hock, *Z. Elektrochem.* **31**, 404 (1925).
[46] Hock, in Memmler, "Science of Rubber", translated by Dunbrook and Morris, Reinhold Publishing Corp., New York, **1934**, p. 421.
[47] Thiessen and Kirsch, *Naturwissenschaften* **26**, 387 (1938); RUBBER CHEM. TECH. **12**, 12 (1939).
[48] Thiessen and Kirsch, *Naturwissenschaften* **27**, 390 (1939); RUBBER CHEM. TECH. **13**, 48 (1940).
[49] Smith, Saylor and Wing, *Bur. Standards J. Research* **10**, 479 (1933); RUBBER CHEM. TECH. **6**, 351 (1933).
[50] Katz and Bing, *Z. angew. Chem.* **38**, 439 (1925).
[51] Katz, *Naturwissenschaften* **13**, 410 (1925).
[52] Park, *Mem. Coll. Sci Kyoto Imp. Univ.* **A22**, 13 (1939); *J. Soc. Chem. Ind. Japan* **12**, 462 (1939); RUBBER CHEM. TECH. **12**, 778 (1939).
[53] Smith and Saylor, *J. Research Natl. Bur. Standards* **13**, 453 (1934); RUBBER CHEM. TECH. **8**, 214 (1935).
[54] Smith and Saylor, *J. Research Natl. Bur. Standards* **21**, 257 (1938); RUBBER CHEM. TECH. **12**, 18 (1939).
[55] Bunn and Garner, *J. Chem. Soc.* **1942**, p. 654; RUBBER CHEM. TECH. **16**, 848 (1943).
[56] Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934); RUBBER CHEM. TECH. **8**, 5 (1935); Cotton, *Trans. Inst. Rubber Ind.* **16**, 303 (1941); RUBBER CHEM. TECH. **14**, 762 (1941).
[57] Meyer, Von Susich and Valko, *Kolloid-Z.* **59**, 208 (1932); Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934); RUBBER CHEM. TECH. **8**, 5 (1935); Hock, in Memmler, "Science of Rubber", translated by Dunbrook and Morris, Reinhold Publishing Corp., New York, **1934**, p. 421; Park, *Mem. Coll. Sci. Kyoto Imp. Univ.* **A22**, 13 (1939); *J. Soc. Chem. Ind. Japan* **12**, 462 (1939); RUBBER CHEM. TECH. **12**, 778 (1939); Thiessen and Kirsch, *Naturwissenschaften* **27**, 390 (1939); RUBBER CHEM. TECH. **13**, 48 (1940); Cotton, *Trans. Inst. Rubber Ind.* **16**, 303 (1941); RUBBER CHEM. TECH. **14**, 762 (1941); Bunn and Garner, *J. Chem. Soc.* **1942**, p. 654; RUBBER CHEM. TECH. **16**, 848 (1943).
[58] Bunn, *Trans. Faraday Soc.* **38**, 372 (1942); RUBBER CHEM. TECH. **15**, 704 (1942); **16**, 775 (1943).
[59] Treloar, *Trans. Faraday Soc.* **36**, 538 (1940); RUBBER CHEM. TECH. **13**, 795 (1940).
[60] Wood, *J. Chem. Physics* **10**, 403 (1942).
[61] Tammann and Jenckel, *Z. angew. allgem. Chem.* **193**, 76 (1930); Volmer and Marder, *Z. physik. Chem.* **A154**, 97 (1931); Tammann, "Der Glaszustand", Leopold Voss, Leipzig, 133; Goetz and Goetz, *J. Applied Physics* **9**, 718 (1938); Avrami, *J. Chem. Physics* **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941); Gehman and Field, *J. Applied Physics* **10**, 564 (1939); RUBBER CHEM. TECH. **12**, 706 (1939) Johnson and Mehl, *Trans. Am. Inst. Mining Met. Eng.* **135**, 416 (1939).
[62] Von Goler and Sachs, *Z. Physik* **77**, 281 (1932); Avrami, *J. Chem. Physics* **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941); Wood, in "Advances in Colloid Science", edited by Mark and Whitby, Interscience Publishers, Inc. New York, **1946**, Vol. 2, p. 57.
[63] Alfrey and Mark, RUBBER CHEM. TECH. **14**, 525 (1941); *J. Chem. Physics* **46**, 112 (1942); RUBBER CHEM. TECH. **15**, 462 (1942); Mark, *Ind. Eng. Chem.* **34**, 449 (1942); RUBBER CHEM. TECH. **15**, 452 (1942).
[64] Bunn, *Proc. Roy. Soc. London*, **A180**, 40 (1942); RUBBER CHEM. TECH. **15**, 709, (1942); *Proc. Roy. Soc. London* **A180**, 82 (1942); RUBBER CHEM. TECH. **15**, 742 (1942); *Trans. Farday Soc.* **38**, 372 (1942); RUBBER CHEM. TECH. **15**, 704 (1942); **16**, 775 (1943).
[65] Treloar, *Reports on Progress in Physics, Phys. Soc. London*, **1943**, Vol. 9, p. 113.
[66] Wood, In "Advances in Colloid Science", edited by Mark and Whitby, Interscience Publishers, Inc., New York, **1946**, Vol. 2, p. 57.

TACKINESS OF GR-S AND OTHER ELASTOMERS *

W. F. Busse, J. M. Lambert, and R. B. Verdery

General Aniline and Film Corporation, Easton, Pennsylvania

I. INTRODUCTION

Tackiness is usually measured by hand tests, which are very simple to apply but which are very complex because they involve an unconscious integration of a great many factors. The particular combination of properties which produces tack in one system, such as printing inks, may be quite different from the combination which produces tack in another system such as rubber, even though the overall effect as measured by hand tests may be the same. Hence it is not surprising that there is little agreement as to the factors involved in producing tackiness of different materials and that very few quantitative methods of measuring tackiness have been developed.

This paper presents an analysis of the operation of measuring tack, to make explicit some of the detailed factors involved, both in the materials and in the testing operation. Methods of measuring the effects of some of these different factors have been developed and applied to the study of the "tackiness" of such materials as pressure-sensitive adhesive tapes and various elastomers, including polyvinyl ethers and natural and synthetic rubbers.

The magnitude of the "tackiness" of a material (as measured by the resistance to the separation of two surfaces which have been brought in contact), depends on the geometry or roughness of the surface of the sample, as well as on the surface adhesive forces and the visco-elastic properties of the material, and the relation of these factors to the time of application and magnitude of the force pressing the surfaces together. Hence, the results of quantitative tests of "tackiness" are not in any sense absolute properties of the material. However, they do give better measures of tackiness than can be obtained by hand tests, and they make possible more precise studies of the effects of some processing conditions and compounding agents on the tackiness of GR-S and natural rubbers.

II. HISTORY

Studies of the properties that produce "tack" in viscous liquids were made as early as 1847 by Stefan[1] and somewhat later by Reynolds[2]. Both considered tackiness to be measured by the force required to separate, at a given rate, two flat disks immersed in the liquid, and they developed equations for relating the applied force to the times of separation, assuming the laminar flow of Newtonian liquids. Later similar formulas were developed[3], some of which[4] were modified to take account of the yield value of the materials. Recently it has been shown[5] that tack of printing inks correlates well with the viscosity measured at high rates of shear.

Little work has been done to relate tackiness to molecular properties, but it was pointed out[6] that tackiness as well as "stickiness", and the ability of

* Reprinted from the *Journal of Applied Physics*, Vol. 17, No. 5, pages 376–385, May 1946.

polymeric materials to be drawn into fibers, seems to be correlated with a relaxation time of 10^{-7} to 10^{-4} second, or a viscosity of 10^2–10^4 poise, and a linear chain length of about 100 links.

It has been emphasized[7] that in the case of rubber "autohesion", or the sticking together of two like surfaces when brought in contact, is an important factor in tackiness. The relations of various fundamental properties to the tackiness of paints, inks, rubbers, etc., were discussed by a number of authors at a recent meeting of the British Rheologists Club[8]. In this discussion Scott emphasized two factors which are important in producing a bond between the two surfaces[9]:

(1) getting the two surfaces into contact; and
(2) mutual "fusion" of the surface layers.

Phase (1) of the process is greatly influenced by the roughness of the rubber surfaces. Phase (2) for rubberlike materials is thought to involve a rapid interpenetration, *i.e.*, self-diffusion of at least parts of the long rubber molecules composing the two surface layers.

The rheology of rubber is of great importance, since it must deform readily (at least on the surface) under small stresses to produce close contact of the two surfaces. It is interesting that this requirement of ease of deformation for good tack is just opposite to the requirement for so-called tacky adhesion between the two plates separated by a layer of viscous or plastic material considered by Stefan[1] and Reynolds[2].

Experience with GR-S shows that the addition of resinous materials and various other softeners to rubber often makes it "stick" to mill rolls, liners, etc., without giving it the combination of surface and bulk properties required for good autohesion or "tack". Extensive studies have been made and published in this country[10] on the effect of various softeners and "extenders" on the physical properties of GR-S, without finding materials which gave synthetic rubber the tack of natural rubber. All measurements of tack were based on hand tests.

The report of the committee investigating the German Rubber Industry[11] indicates that one of the few worthwhile advances made by the German rubber industry during the war was the development of Koresin as a tackifier of butadiene-styrene rubber. This was reported to give rubber excellent tack, but no quantitative data were obtained.

III. ANALYSIS OF "TACKINESS"

Before trying to measure quantitatively the tackiness of synthetic rubbers, it is helpful to analyze in detail the operation of measuring tack, to determine some of the different kinds of factors which are involved. This operational method of analyzing the process leads to a recapitulation and organization of many of the factors which have been suggested in the literature and to the recognition of some additional factors.

Expressed in the simplest terms, the operation of determining tackiness consists of:

(1) *Producing contact between two surfaces for a short time by the application of a force, and*

(2) *Separating the surfaces and noting the force required.*

The force applied to separate the surfaces is the "tackiness" under the particular conditions used. Since most tack tests have been made by hand, this implies that the magnitude of the adhesion force on the area tested (usually

of the order of 1–10 sq. cm.) should be great enough to be detected by the tactual sensations of the hand. Mechanical tests, however, can extend the concept to a much wider range of values. Further consideration shows that each of these operations can be broken down into a number of simpler factors, as follows.

A.—*Producing contact between two surfaces.*

The amount of surface brought into "molecular contact" in a given area depends on:

1. Initial roughness of the surface. This determines the magnitude of the deformations required to bring the surfaces into "contact", *i.e.*, within the range of the molecular forces in the surface, or within, say, about 10^{-5} cm.

2. Forces acting to bring the surfaces together. These include:

(a) External forces applied to the material. These usually range from about 1 gram to 1 kg. per sq. cm. of nominal area, and they may act for times ranging roughly from a few seconds to a minute. Occasionally we are interested in the behavior of a material when surfaces are brought together under pressure for times up to weeks or months, as when bales or sheets of a plastic are piled together in storage. Sealing of the surfaces under these conditions is sometimes called "blocking".

(b) Molecular forces at the surface of the material. These short range forces come into play only when the surfaces are in very close contact. They are usually greatest for polar materials, as indicated by the fact that such materials have the highest surface tension in the liquid state. While many of the most tacky materials are polar (asphalt, (warm) rosin, paint, polyvinyl ethers, etc.), the presence of polar molecules is neither necessary nor sufficient for tackiness. Some materials such as polyisobutylene are not polar but are very tacky, while rosin in the solid state is hard and brittle, rather than tacky. In multicomponent systems, tackiness may be determined by the molecular forces of the component that diffuses or blooms to the surface in the highest concentration.

3. Resistance of the material to the deformation required to bring the two surfaces into molecular contact. This involves the visco-elastic properties of the material for deformations of both:

(a) a relatively large scale, required to overcome the gross surface roughness of the material, and

(b) a very small scale, required to produce molecular contact between even smooth surfaces. Since the molecular forces have such short range, the presence of even a small amount of dust may prevent large fractions of the surfaces from coming close enough to be within the range of their cohesive force unless these small scale deformations can be made very easily.

It should be noted that the modulus, or the resistance to deformation, for these very small scale deformations at the surface may be very much higher or very much lower than the modulus for large deformations of the whole sample. A very thin layer of hard oxidized material might greatly increase the modulus of the surface layer, while the blooming of a small amount of liquid component to the surface might reduce the modulus of this layer. It is possible that the presence of small regions of rigid gel structure at the surface of GR-S might tend to prevent the molecular contact needed to produce good tack.

The relaxation times of material in the surface layer and the bulk material determine the length of time the forces must act to produce the required deformations.

B.—*Separating the surfaces and noting the force required.*

This factor depends on:

1. The magnitude of the molecular forces per unit area of molecular contact, and on the total area of such contact.

2. The ultimate tensile strength of the material for the particular kind and rate of applied stress.

It is this factor which keeps liquids such as water from being tacky. Water is easily deformed, makes good molecular contact with other surfaces brought into contact with it, and it has high surface forces, but it does not have sufficient tensile strength or viscosity to resist separation, even at high speeds. In the case of viscous liquid materials like tars, printing inks, etc., the "tensile strength" may in effect be merely the viscous resistance to deformation. Here the "tensile strength" depends very much on the rate of deformation.

3. The distribution of the applied stress and resultant elongations. This determines the magnitude of the force which must be applied to stress the material to its "tensile strength" at the line of separation. This depends on:

(a) The geometry of the sample, *i.e.*, the thickness, area, and shape, and the position and direction of application of the applied force. This may be applied normal or parallel to the surface, or to produce pealing apart of the materials along a line, producing various kinds of stress gradients.

Since in tack tests the separating force is applied in such a way as to produce a stress gradient in the sample, the total force depends very much on the ultimate elongation of the material, for this affects the total volume of material that must be stretched.

It should be noted that, under some conditions, the force applied to remove the samples may result in two- or even three-dimensional tensile stresses in the sample. The behavior of the sample to such stresses may be quite different from its behavior under a one-dimensional tensile stress, just as is the case in tensile and tear tests of cured rubber[12]. As a rule, the most tacky materials react to this complex stress pattern by forming irregular "teeth" or "legs" in the region of separation.

(b) The stress-strain-relaxation properties of the material.

General experience suggests that the differences in apparent tack which are found by varying the conditions under which the surfaces are separated (*e.g.*, at different rates of separation, temperature, etc.) probably are due to changes in the stress distribution in the region of separation, resulting from the differences in the apparent effective visco-elastic properties of the medium.

Two sheets of milled rubber, for example, which are stuck together so firmly that they tear along new surfaces when pulled apart slowly, can sometimes be separated along the original surfaces by a very quick pull. This in effect makes the rubber much stiffer and stronger, and thus puts relatively more stress on the bond between the surfaces.

IV. MEASUREMENT OF TACKINESS

(1) EFFECT OF TESTING CONDITIONS ON TACK OF ADHESIVE TAPES

The properties which affect tack (or resistance to separation) such as modulus, elongation, and plastic deformation, vary with both time of application of force, and temperature of the material. Therefore, a complete description of the tackiness of a material should include data for a wide range of time of contact of load and rate of separation of surfaces, preferably also over a wide range of temperatures.

To get some quantitative data on the importance of the rate factor, measurements were made of the relation between the applied load and the rate of removal of pressure sensitive adhesive tapes from glass surfaces, since this makes the factor of surface roughness small and constant.

The simplest method used to measure this relation was to put a number of strips of adhesive tape ½ inch wide by about 12 inches long (1.25 cm. × 30 cm.) on the bottom of a 10 by 15 inch (25 cm. × 37 cm.) plate of glass held horizontally in a rack, and hang known loads from the free ends of each tape to pull it away from the glass. This method had the advantage that it could be used in an oven to get data at elevated temperatures, and a number of tapes and loads could be tested at any one time. It had the disadvantage that, particularly at low loads, nonuniformities in the tape might make the rate of removal irregular, or even stop it altogether. However, the test gives considerable more information about the adhesive properties than a test which measures only the force required to remove the tape at one rate.

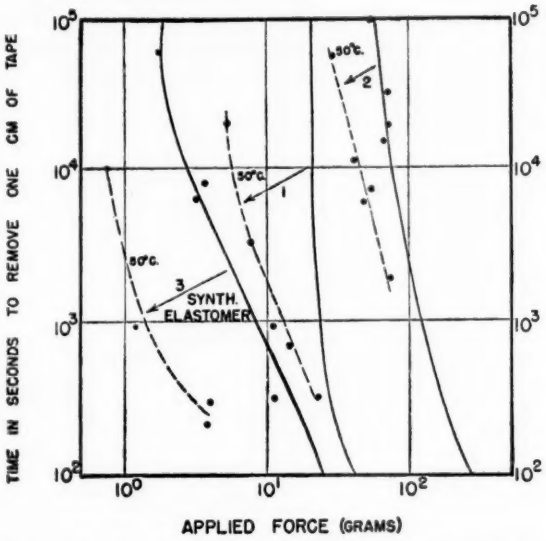


FIG. 1.—Relation of applied force to rates of removal of adhesive tapes.

Data obtained with this test for three samples of experimental pressure-sensitive adhesive tapes at room temperature and 50° C are shown in Figure 1. Tape No. 1 was made from GR-S, No. 2 from natural rubber, and No. 3 from an experimental synthetic elastomer base[13]. Since each tape contained various amounts (not necessarily the optimum) of plasticizer and tackifier, the results illustrate the physical properties that can be obtained in tapes, rather than the fundamental properties of specific elastomers. Because of the long times involved, the removal of the tapes are expressed as reciprocal rates, or seconds per cm.

At room temperature tape No. 3 supported a load of 1.8 gram indefinitely (10^5 seconds to remove 1 cm.) but it required about 27 grams or a 15-fold increase to remove it at the rate of 10^2 seconds per cm. The tape made with natural rubber held a load of 20 grams indefinitely, but 40 grams removed

the tape at 10^2 seconds per cm., or a range of only two-fold, which is very desirable. The GR-S tape supported larger loads, but about a five-fold range of loads was required to change the reciprocal rate of removal from 10^5 seconds per cm to 10^2 seconds per cm.

The loads required to remove the tapes at a given rate at 50° C are seen to be only about one-half to one-fifth those required at room temperature, but not enough data are available to draw any theoretical conclusions from the temperature coefficient.

To avoid some of the difficulties of this first test, equipment was built by F. E. Wetherill of this laboratory to remove the tapes at definite rates over

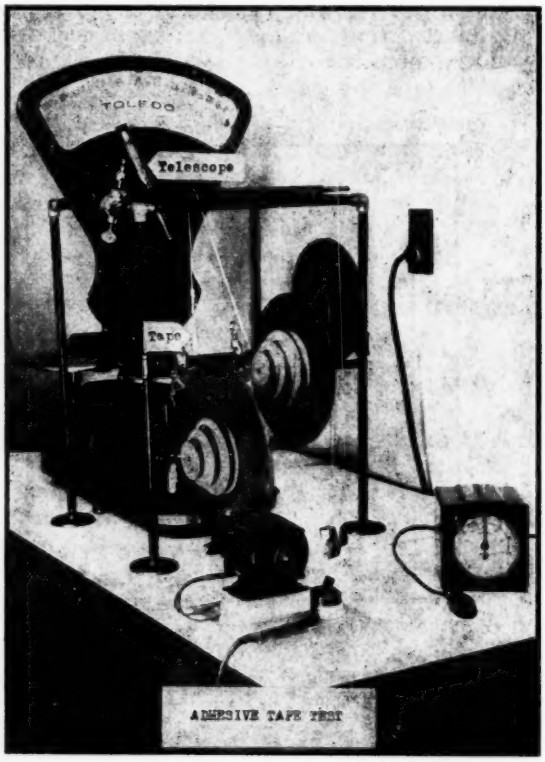


FIG. 2.—Adhesive tape test.

nearly a 10^6-fold range and measure the force applied. This was done by fastening the glass plate to the pan of a direct reading scale that read from 1 to 1000 grams. The adhesive tape, 1.2 cm. (0.5 in.) wide by about 25 cm. (10 in.) long, was fastened to the top of the glass plate, and the free end of the tape was pulled normal to the surface by means of a cord which passed over a roller about a foot above the tape, and then went around another pulley which was driven at the desired speed.

The wide range of driving speeds required was obtained very simply by a train of multiple pulleys made from wood and fiber board. They were mounted

so that, for example, the large pulley of each unit could be driven by friction from a smaller pulley of the preceding unit. By changing the number and diameter of the pulleys used in the train, and using a motor with built-in speed reducer, the speed of removal of the tape could be varied from about 10^{-1} to 5×10^4 seconds per cm.

The amount of tape removed in a given time interval was read with a small telescope from a metal scale placed on the balance pan beside the tape. A picture of the equipment is shown in Figure 2.

Typical results from this test are shown in Figure 3 which gives data on experimental tapes. The elastomers are No. 1, natural rubber, No. 2, GR-S,

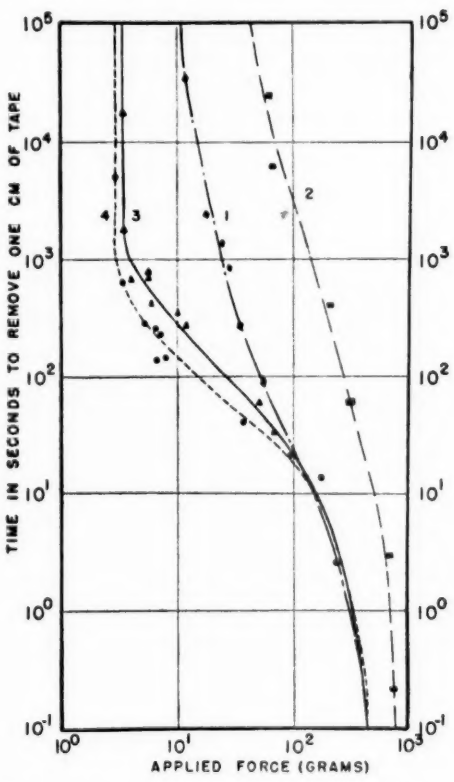


FIG. 3.—Relation of applied force to rates of removal of adhesive tapes.

No. 3, and No. 4, two other synthetic elastomers. Again the data illustrate only the behavior of the particular tapes rather than fundamental properties of the elastomers.

It is apparent that tapes Nos. 1, 3, and 4 have about the same properties if tested at relatively high rates of removal—say, from 0.1 to 5 seconds per cm. removed (10 to 0.2 cm. per second). At very low rates of removal, however, they were quite different. Tapes Nos. 3 and 4 were removed slowly at loads above about 3.3 grams, while the rubber base tape did not start to be removed until the load was over 10 grams. The behavior at these low rates of removal

is important wherever pressure-sensitive tapes are used to seal packages, or to hold objects on a wall, etc., as they are then subject to small stresses for long times, and their performance in service may be determined by this factor. Tapes such as No. 3 and No. 4 failed on such service tests while No. 1 was satisfactory. The tape No. 2 had good adhesion to the glass, but other properties made it less satisfactory than No. 1.

(2) TACKINESS TEST FOR NATURAL RUBBER AND GR-S

a. Discussion of Test

The test used in this work was designed primarily to give a quantitative measure of the effect of various materials on the tackiness or resistance to separation of sheets of GR-S under conditions approximating those of the hand test. The method could easily be modified to study the effects of varying the magnitude and time of application of the compression force, the rate of separation of the surfaces, etc. However, this was not found necessary for the evaluation of compounding ingredients and milling conditions on the tackiness of GR-S.

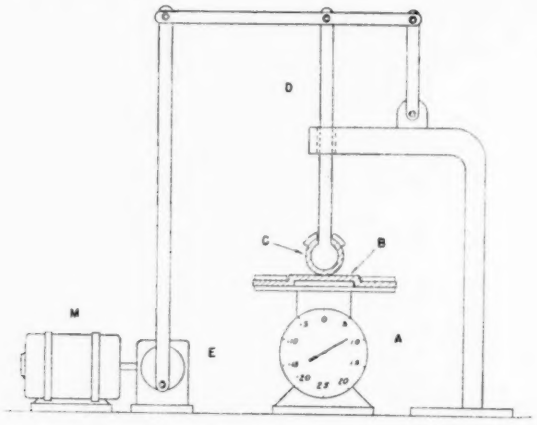


FIG. 4.—Schematic diagram of tackiness tester.

An obvious difficulty in developing a quantitative test of the tackiness of rubber is to get samples with reproducible smooth, uniform surfaces. A number of ways of doing this have been suggested, including molding smooth samples, depositing the rubber from solution, calendering the rubber onto fabric, etc., but they all have the disadvantage of changing the rubber to be tested.

A closer examination of the problem shows, however, that surface roughness is not necessarily as serious a problem as it first appears. Since it has been possible in practice to ignore this factor in hand tests, it is evident that, by standardized preparation of the sample, surfaces of at least approximately reproducible roughness can be obtained. It was found possible to use rubber samples 2–3 mm. thick prepared by milling sheets on a small (2 × 6 inch) laboratory mill (made by Wm. R. Thropp and Sons). Uncompounded GR-S gave the most irregular samples, but on adding 45 parts EPC black to 100 parts GR-S the magnitude of the irregularities was reduced, and the sheets appeared

more uniform. However, even the uncompounded GR-S could be prepared in fairly reproducible sheets.

To measure the tackiness, the equipment shown schematically in Figure 4 was used. One strip of the rubber to be tested, *B*, at least 3 × 5 cm. (1.2 × 2 inches) is fastened to the pan of a preloaded spring scale, *A*, which reads compression and tension loads directly. Another sample, *C*, of the rubber is put around a mandrel 3.4 cm. (1½ inches) in diameter and 2.5 cm. (1.0 inch) wide and lowered by the motor *M* through the drive *B*, in a 2.4-second cycle.

The sample *C* is pressed against *B* with a force of 565 grams (20 oz.) at the bottom of the stroke and then pulled away. The maximum position of the scale pointer on the return stroke is read. This value, when corrected for the inertia effects of the system, is a measure of the force required to separate the samples, or the "tackiness", for "instantaneous" loading. At least five tests are made at different places on the surface and averaged for the "instantaneous tack" values.

The motor driving the mandrel can be stopped at the bottom of the cycle to leave the samples in contact under load for any desired time, and the motor then restarted. The force required to separate the samples after the load is applied for 10 seconds is called the "10-second tack". Five readings of this are taken and averaged.

Usually the "instantaneous tack" and the "10 second tack" values changed more or less parallel with each other, so the two values are averaged in this report unless otherwise noted. In a few cases, where the samples sealed and could not be separated after the load was on for 10 seconds, only the instantaneous values are given. The average tack values for any one sample are reproducible to within about ±30 grams.

Because the initial rubber and the details of processing were different in different series of tests, the absolute values of tackiness in different series cannot be compared. Within each series, however, the data are comparable.

b. Effect of Some Processing Conditions on Tack of Natural Rubber and GR-S

It is known that natural rubber breaks down (due to oxidation) and becomes soft and plastic more rapidly when milled on a cold mill (20° C) than when milled on a warm or hot mill[14] (100° C), so it might be expected that cold milling would make the rubber more tacky than hot milling. The following test (Table I) shows that this result is not always obtained.

Samples of pale crepe were milled at 25° and 60° on a 2 × 6 inch mill, the temperatures of the rubber being measured by a thermocouple. The tack

TABLE I

EFFECT OF MILLING ON TACK OF PALE CREPE.

Sample	Treatment	Temp. (°C)	Time (min.)	Separating force (grams) after 1–2 hr.	Separating force (grams) after 24 hr.	Appearance of sample after milling
I	Initial milling	60	8	525	185	Smooth
Ia	I remilled	25	7	115	—	Creped-rough
Ib	I remilled	60	7	405	—	Smooth
II	Initial milling	25	3	30	35	Creped-rough
IIa	II remilled	25	3	35	—	Creped-rough
IIb	II remilled	60	5	330	—	Smooth
III	Initial milling	25	15	105	110	Creped-rough
IIIa	III remilled	25	15	600	—	Smooth

values or separating force (grams) were measured within 1–2 hours and after 24 hours. Samples given the initial hot milling were then remilled at 60° and at 25° C. Some of the samples were so tacky that the surfaces sealed when pressed together for 10 seconds, so all of the tack values of Table I are for the separating force in grams after the "instantaneous" load.

The results shown in Table I agreed qualitatively with the hand tests of the tack of these samples. They suggest that the difference in tack of the hot- and cold-milled samples is largely due to the physical state of the surface. The samples which were cold milled for a short time had rough creped surfaces which prevented intimate contact over large areas, so gave low values for the tackiness. The hot-milled samples, and the samples cold milled for 30 minutes had smooth surfaces which allowed good contact and so gave very high tack values. The decrease in tack of sample I on standing 24 hours may be due in part, at least, to the development of surface roughness on standing.

The results show that the tackiness measured in this test is not an absolute property of the material. However, it does appear to measure a combination of properties of the material and the sample geometry which is important both in the hand tack test, and in "adhesion" of plies in actual factory processing.

When GR-S was milled on the small mill, its tack was low for all milling temperatures from 15 to 70° C, as shown in Table II. The tack was somewhat

TABLE II

EFFECT OF MILLING TEMPERATURE ON RELATIVE TACK OF GR-S

Tempersture (°C)	15	30	50	70
Separating force (grams)	155	85	30	10

higher for samples milled cold, but varying the milling time from 5 to 15 minutes, had little if any effect on the tack. Samples of GR-S from different sources gave some variation in tack values, but none were very tacky.

When GR-S and a stock containing GR-S 100 parts, and EPC black 45 parts, were masticated for various times in a Midget Laboratory Banbury mixer, the results shown in Table III and Figure 5 were obtained. The samples marked "hot" were run with steam (100° C) through the jacket and cold water through the rotor, and those marked "cold" were run with cold water (20° C) circulating through the jacket and rotor. 250 grams of rubber were used and 30-gram samples were removed for test after various times of mastication.

TABLE III

EFFECT OF MASTICATION TIME ON TACKINESS AND PLASTICITY OF GR-S

Composition	Masticated (min.)	Separating force (grams) when masticated		Williams plasticity (100° C) when masticated	
		Hot	Cold	Hot	Cold
GR-S	5	215	160	2.9	3.0
	10	285	200	2.7	2.8
	20	425	285	2.3	2.7
	30	525	300	2.1	2.5
	45	640	315	1.8	2.4
GR-S and EPC black	20	115	55	4.4*	4.1
	30	115	55	4.2*	3.8
	45	140	85	3.9*	3.7
	60	170	85	3.8*	3.5

* Plasticity values after 9 days.

For the stock containing carbon black the rubber was broken down for 5 minutes and the carbon black was then added and mixed 15 minutes when the 20-minute sample was removed. Each sample was then milled 2 minutes on the 2 × 6 inch mill to sheet out, the rubber samples being milled at 20° C and the black samples at 600° C. Tack tests and Williams plasticity tests at 100° C were made after 24 hours, except for one group of plasticity tests made after standing for a longer time. The plasticity figures are the thickness in mm. of the 2-cc. sample after being subject to the 5-kilogram load for 3 minutes. The tack values are the average of "instantaneous" and "10-second" tests for each of two independent series of mastication tests.

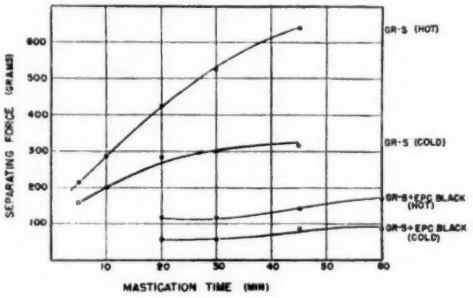


FIG. 5.—Effect of mastication time on tackiness of GR-S.

It is seen that in these tests the hot Banbury mastication consistently gives somewhat tackier and more plastic samples than the cold mastication, even with the stock containing 45 parts EPC black. Increased mastication time increases the tack readings, in part because it makes the samples softer. This method of increasing tackiness may not be practical, however, because of the excessive time of mastication required and the deleterious effects of high temperature on the properties of the cured compounds[15].

c. Effect of Vinyl Ethers on Tackiness of GR-S

Since some of the polyvinyl ethers are extremely tacky materials themselves, it was thought that they might improve the tackiness of GR-S. A series of polyvinyl ethers[16] of different molecular weights (viscosities) was tested by milling 10 parts each into 100 parts GR-S on the 2 × 6 inch mill run hot (60° C). The results are shown in Table IV.

TABLE IV

EFFECT OF POLYVINYL ISOPROPYL ETHERS ON TACKINESS OF GR-S

Sample	Specific viscosity*	Separating force (grams)
1	0.05	50
2	0.13	160
3	0.63	330
4	0.84	310
5	2.13	280
Control (GR-S only)	—	30

* In 1 per cent benzene solution.

The results show that, within the proper molecular weight range, these vinyl ethers do produce tackiness in GR-S, but the lower molecular weight ethers were not effective. On the same test, 10 parts of rosin oil in 100 parts GR-S did not produce a measurable increase in the tackiness.

The vinyl ethers are not very compatible with the GR-S rubber, so they probably tend to bloom to the surface and thus make the surface tacky. Compounded stocks containing vinyl ethers can be piled up and cured satisfactorily to a solid piece. However, if two samples are painted with a solution of vinyl ether, and pressed together during cure, they do not fuse together and the cured samples can easily be separated.

d. Effect of Koresin and Other Tackifiers on GR-S

When reports reached this country that Germany had developed a product that was a very effective tackifier of their Buna-S, the Rubber Reserve Company took steps to find its composition and to get a source of supply in this country. The material was found to be a reaction product of acetylene and *p-ter*-butylphenol. The Rubber Reserve Company made arrangements to have this product, known as Koresin, made in this country[17] and samples supplied to the rubber industry.

The results obtained when various amounts of Koresin were mixed in GR-S and in a stock containing GR-S 100 parts and EPC black 45 parts are shown in Table V and Figure 6. The mixing was done for 5 minutes in the small Midget

TABLE V

EFFECT OF MIXING KORESIN INTO GR-S

Stock	Parts Koresin	Separating force (grams) after standing for		
		1–2 hr.	24 hr.	1 week
GR-S	0	200	170	200
	5	540	570	570
	10	650	710	650
GR-S and EPC black	0	55	55	85
	5	395	340	340
	10	455	480	455
	15	595	425	510

Laboratory Mixer run hot, and the samples were then sheeted out for 5 minutes by milling on a warm (60° C) 2 × 6 inch mill. The tackiness was measured after the samples stood various times up to a week in an air-conditioned room 75° F-30 per cent relative humidity.

It is seen that 5–15 parts Koresin per 100 GR-S are very effective in increasing the tack of both GR-S above and of GR-S containing 45 parts black, and that the tack decreases only slightly on standing for one week. However, if the samples are stored at high humidities or where water gets on the surface, the tack drops more rapidly. The addition of Koresin has no deleterious effect on rate of cure, or tensile properties of the cured GR-S compounds.

When Koresin is applied as a solution or cement to the surface of a stock containing GR-S 100 parts and EPC black 45 parts, the results depend very much on the concentration used. Table VI and Figure 7 show the results of two series of tests—one studying the effect of various concentrations of Koresin solution in hexane, and the other comparing Koresin with other materials when applied as solutions in hexane.

There is a definite optimum at around 3–4 per cent concentrations of Koresin solution This tends to confirm the view that Koresin increases the tack of GR-S in part, at least, because of its tendency to bloom to the surface, forming a layer of high Koresin concentration. When a large excess of Koresin is present, however, the Koresin seems to form a "lacquer" on the surface which is dry, hard, and nontacky.

If the solutions are applied in atmospheres of very high humidity, where moisture can condense on the surface, the tackiness is very much reduced. The mechanism of this action is not known, but a similar effect is noted with rubber cements.

A comparison of a number of different softeners and tackifiers added in the Midget Banbury Mixer to a stock containing GR-S 100 parts and EPC black

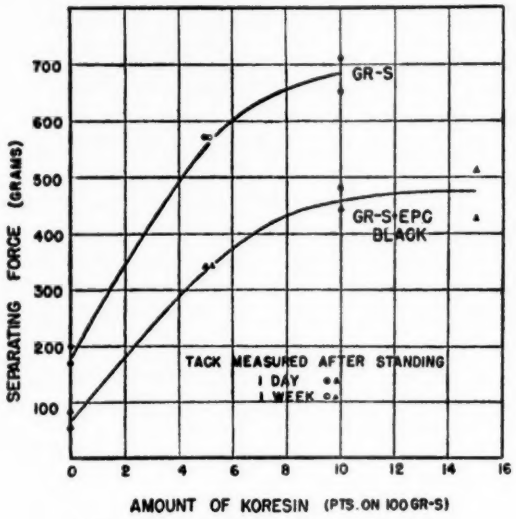


Fig. 6.—Effect of mixing Koresin into GR-S.

Table VI

Effect of Painting Various Materials on Surface of GR-S Carbon Black Compound

Material	Concentration (%)	Separating force (grams) after 1 hr.	3 hrs.	24 hrs.	1 week
Series 1.					
Solvent only	—	55	—	55	—
Koresin	1.0	255	—	115	—
Koresin	2.0	310	—	200	—
Koresin	4.0	310	—	310	—
Koresin	5.0	255	—	255	—
Koresin	10.0	30	—	30	—
Koresin	15.0	30	—	30	—
Series 2.					
Koresin	3	255	225	255	140
Koresin (German)	4	225	170	140	140
GR-S	4	115	85	85	85
Natural rubber	4	370	225	170	55
Dehydroabietic acid	4	170	140	85	55

45 parts is shown in Table VII. The plasticity values are taken after 24 hours, on the Williams Plastometer at 100° C.

It is seen that 10 parts of Koresin gives the most tack of any material tested. A mixture of equal parts of Koresin plus the petroleum derivative (Circosol-2XH) (10 parts total) is almost as effective as 10 parts Koresin, even though 10 parts of the petroleum derivative alone has little effect on the tackiness. The tackiness of the Koresin stocks does not decrease markedly in a week when stored in an atmosphere at 75° F and 30–35 per cent relative humidity.

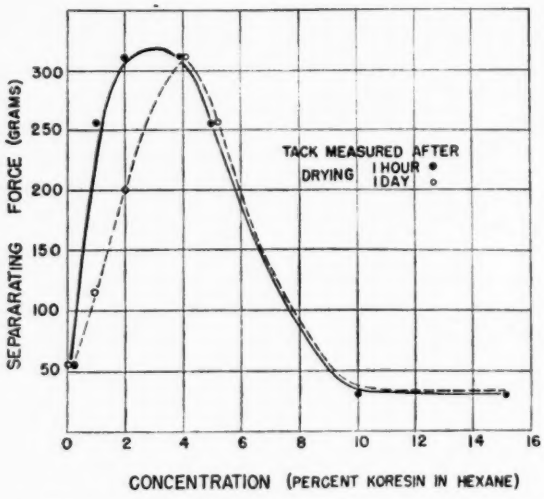


FIG. 7.—Effect of painting Koresin solutions (hexane) on surface of GR-S carbon black compound.

TABLE VII

EFFECT OF VARIOUS MATERIALS ON THE TACKINESS OF GR-S EPC BLACK COMPOUND

Material added	Amount added (on 100 parts GR-S)	Separating force (grams) after standing for 1–2 hrs.	1 day	1 wk.	Williams plasticity (100° C)
Control (GR-S compound only)	—	55	55	85	4.3
Koresin	5	395	340	340	3.9
Koresin	10	455	480	455	3.6
Koresin and petroleum deriv. (1:1)	10	480	455	455	3.7
Koresin and coal tar fractions (1:1)	10	425	340	425	3.7
Dehydrogenated rosin	10	370	255	200	3.7
Petroleum derivative	10	170	85	115	4.1
Coal tar fraction	10	170	115	85	3.8
Rosin oil	10	200	115	115	3.7
Stearic acid	10	55	30	55	3.8

CONCLUSIONS

The analysis of tackiness shows that it is a complex property which depends on a balance between a large number of different factors, including the geometry of the sample as well as the surface forces and the visco-elastic properties of the material itself.

The quantitative measurements of the effect of the rate of removal on the apparent tackiness of pressure-sensitive adhesive tapes show that significant differences are found at very slow removal rates (10^5 seconds per cm.) which do not show up at much higher removal rates (10 seconds per cm.). These differences may affect the performance of the tapes in service.

A simple quantitative test is described which can be used to study the effects of various processing treatments and various softeners, tackifiers and other compounding ingredients on the tackiness of GR-S and other rubbers. Koresin was the most effective tackifier found for GR-S.

The authors wish to acknowledge the continued interest of W. E. Hanford, Director of the Laboratory, and the helpful discussions of tackiness measurements with C. E. Schildknecht. Miss Ruth Sellers and Miss J. L. Nuver helped in taking much of the data. The first Koresin samples were prepared in the laboratory by C. E. Schildknecht and A. O. Zoss before the commercial material was available.

REFERENCES

[1] Stefan, *Ber. Kais. Akad. Wiss. Wien* **69**, 713 (1847).
[2] Reynolds, *Phil. Trans. Roy. Soc. London* **177**, 157 (1886).
[3] Haley, *Trans. Inst. Rubber Ind.* **1**, 334 (1926).
[4] Scott, *Trans. Inst. Rubber Ind.* **17**, 169 (1931).
[5] Green, *Ind. Eng. Chem. Anal. Ed.* **13**, 632 (1941).
[6] Josefowitz and Mark, *India Rubber World* **106**, 33 (1942).
[7] Zhukov and Talmud, *J. Rubber Ind.* (U.S.S.R.) **12**, 1005 (1935).
[8] *Rheology Bull.* **16**, 70 (1945); *Paint Tech.* **9**, 211 (1944).
[9] Scott, *Paint Tech.* **9**, 218 (1944).
[10] Ludwig, Sarback, Garvey and Juve, *India Rubber World* **111**, 180 (1944); **112**, 731 (1945).
[11] Summary Report, Rubber Bur. WPB and Office of Rubber Reserve, Washington, Aug. 1945.
[12] Busse, *J. Applied Physics* **9**, 438 (1938).
[13] These were supplied through the courtesy of the Industrial Tape Corp., New Brunswick, N.J.
[14] Busse, *Ind. Eng. Chem.* **24**, 140 (1932); *Proc. Rubber Tech. Conf. London*, 1938, p. 288; Cotton, *Trans. Inst. Rubber Ind.* **6**, 487 (1931).
[15] Wiegand and Braendle, *Ind. Eng. Chem.* **36**, 699 (1944).
[16] Prepared by F. Grosser and C. E. Schildknecht of this laboratory.
[17] By General Aniline and Film Corp., U. S. patent 2,337,464.

STRESS-TIME-TEMPERATURE RELATIONS IN POLYSULFIDE RUBBERS *

M. D. Stern and A. V. Tobolsky

Frick Chemical Laboratory, Princeton, New Jersey

Measurement of relaxation of stress for various hydrocarbon rubbers has been used to investigate the relationships between the physical and structural-chemical characteristics of these materials[1]. The present investigation is an extension of these studies to polysulfide rubbers.

The structures of rubberlike materials have been considered to be three-dimensional networks constructed from long-chain molecules linked at infrequent points. The point where two chains are linked is referred to as a network juncture, and the portion of the long polymer molecule between two junctures is referred to as a network chain. In the unstrained state the network chains tend to assume randomly coiled configurations, the degree of randomness being limited by steric considerations and by interactions with neighboring chains. In the stretched state the network chains of the rubber are forcibly uncoiled, and the stress is calculated from probability considerations in the kinetic theory of elasticity[2] by the equation:

$$f = skT\left[\left(\frac{l}{l_u}\right)^2 - \frac{l_u}{l}\right] \tag{1}$$

where f is the stress on attained section, s is the number of strained elements (network chains) of the structure per unit volume, kT is the thermal energy, and l/l_u is the ratio of stretched to unstretched length.

The network structure must be regarded as a dynamic structure. Strained elements tend to relax their strain because of slippage or rupture at the network junctures or by scission or rupture along the chains. On the other hand, new structural elements (network chains) are always being formed by reformation of bonds or by the formation of new bonds between the chains.

In previous papers[1] it was argued that bond reformation or cross-linking occurs in general in such a way that the network elements thereby formed are relaxed at the moment of formation, and do not contribute to the stress in any configuration of the rubber at which they are formed unless the sample is further strained. For this reason studies of the decay of stress at constant extension isolate the various processes of interchain slippage or rupture at juncture points and (or) bond scission along the network chains. On the other hand, occasional and momentary measurements of the stress required to attain a definite extension, the sample being maintained in an unstrained state between measurements, provide a means of measuring the net rate of bond breakage plus bond reformation through Equation (1). These experiments are referred to as continuous relaxation of stress measurements and intermittent relaxation of stress measurements, respectively. The techniques of these measurements have been previously described.

* Reprinted from the *Journal of Chemical Physics*, Vol. 14, No. 2, pages 93–100, February 1946.

Figures 1 and 2 show intermittent and continuous relaxation of stress data at 130° C for Butyl (polyisobutylene-isoprene) rubber and for Butaprene-NM (butadiene-acrylonitrile) rubber, respectively, the data being plotted as stress divided by initial stress against logarithmic time. These gum vulcanizates have been described in a previous paper[1]. It is apparent from these data that processes of bond scission and bond formation (or cross-linking) are occurring simultaneously in both of these vulcanizates. In the case of Butyl rubber, scission is more rapid, since the intermittent curve shows stress decay, whereas in Butaprene-NM cross-linking predominates because the intermittent curve shows a stress rise. Both scission and cross-linking are caused by the presence of molecular oxygen.

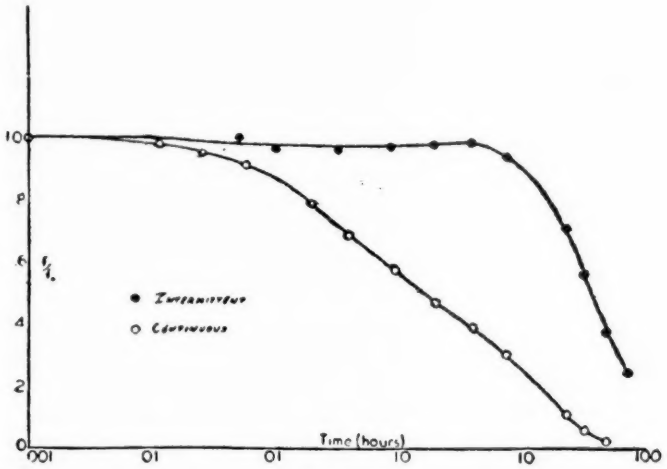


FIG. 1.—Continuous and intermittent stress relaxation of Butyl rubber: 130° C, 50 per cent elongation. ○ continuous, ● intermittent.

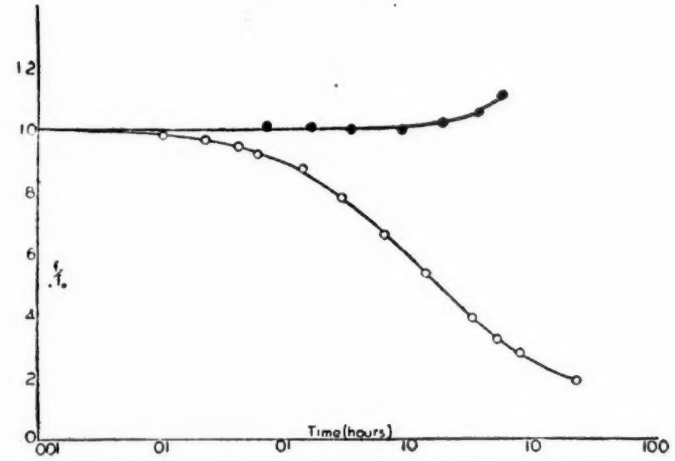


FIG. 2.—Continuous and intermittent stress relaxation of Butaprene-NM: 130° C, 50 per cent elongation: ○ continuous, ● intermittent.

Figure 3 shows similar data for H-11 at 60° C. It is apparent that, inasmuch as the intermittent curve is perfectly flat, the rates of bond breaking and bond formation are exactly equal. This is generally true for all the polysulfide rubbers studied over a wide range of temperature. Furthermore, the bond breaking reaction appears independent of the presence of molecular oxygen from experiments run in high vacuum. From Figure 3 it is apparent that heating in air for times comparable to the relaxation time produces no change in modulus, nor are any other physical or chemical changes observable on visual and manual inspection. Finally, the initial stress required to attain 50 per

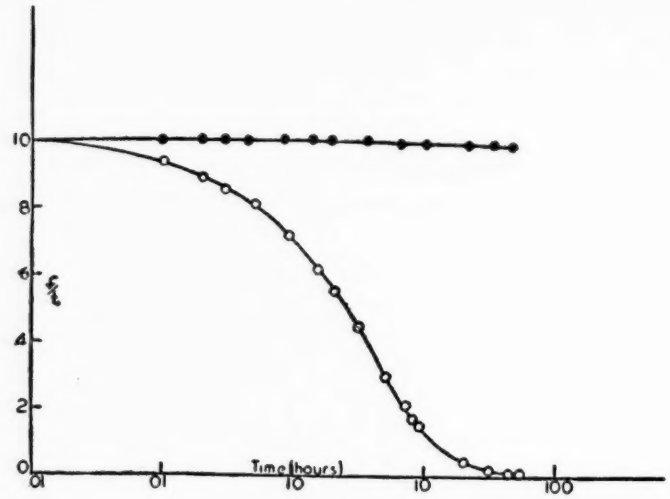


FIG. 3.—Continuous and intermittent stress relaxation of H-11: 60° C, 50 per cent elongation. ○ continuous, ● intermittent.

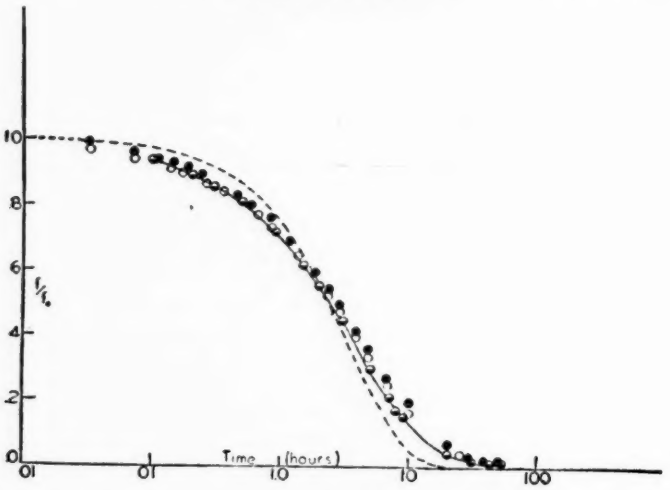


FIG. 4.—Continuous stress relaxation of H-11 at various elongations, and plot of $\exp(-k't)$ at 60° C. ..... $\exp(-k't)$, ● 10 per cent elongation, ○ 30 per cent, ◒ 50 per cent.

cent elongation was found not to vary appreciably over a wide temperature range. For example, for H-11, the initial stress required to attain 50 per cent elongation over a range of temperatures from 30 to 100° C did not vary by more than 1 per cent, which is within the limits of experimental error.

Figure 4 shows the continuous stress relaxation curves of H-11 at 10, 30, and 50 per cent extension and at 60° C, with stress divided by initial stress being plotted against logarithmic time. A dashed curve representing a plot of $\exp(-k't)$ *versus* log time is also shown where k' has been chosen to give the best fit of the experimental relaxation data. It is evident that the effect of elongation on these relaxation curves is very small in this range of elongation, and that the experimental curves closely obey the law:

$$f/f_0 = e^{-k't} \tag{2}$$

It follows from Equation (1) that the rate of stress relaxation caused by slippage at the network junctures or by rupture of bonds along the chain is given by:

$$-(1/s)(ds/dt) = k' \tag{3}$$

where k' may contain, as a multiplicative factor, the number of bonds along the chain susceptible to scission. This simple stress decay law indicates that a single type of bond (with one single rate constant) is responsible for relaxation.

CREEP UNDER CONSTANT LOAD

The behavior of H-11 (which is representative of all the polysulfide rubbers studied), as exemplified in Figures 3 and 4, would appear to indicate that we were dealing with an almost perfect Maxwellian body which obeyed Maxwell's law:

$$ds/dt = (1/G)(df/dt) + (k'f/G) \tag{4}$$

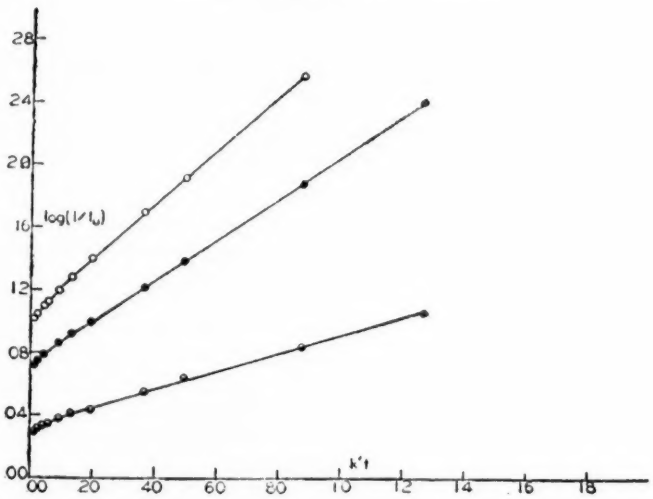


FIG. 5.—Creep curves of H-7 at 60° C l = extended length at time t, l_u = unextended length, l_0 = initial extended length: k' is obtained from stress relaxation data at 60° C. Log_{10} *vs.* $k't$, ○ l_0 = 25.1 per cent, ● l_0 = 16.9 per cent, ◒ l_0 = 6.5 per cent.

where ds/dt is rate of strain, f is stress, G is an elastic modulus, and k' a relaxation rate. Equation (4) would quantitatively explain the results shown in Figures 3 and 4 and Equation (2). However, since Equation (1) indicates that the elastic stress-strain law is not linear (non-Hookean spring) it is clear that Equation (4) could not be an exact representation of all the elastic viscous behavior of polysulfide rubbers, even were we to overlook the slight disparity in the fit of the relaxation curve to $e^{-k't}$. Results on creep, obtained by a previously described method[3], bear this statement out very strikingly. Whereas the Maxwell Equation (4) would predict a linear creep with time, the experimental data (Figures 5 and 6) indicate a creep whose time dependence is even stronger than exponential. This cannot be accounted for in terms of changing cross-section alone, but rather must be interpreted in terms of Equation (1). A complete discussion of the theory of creep will appear in an accompanying article.

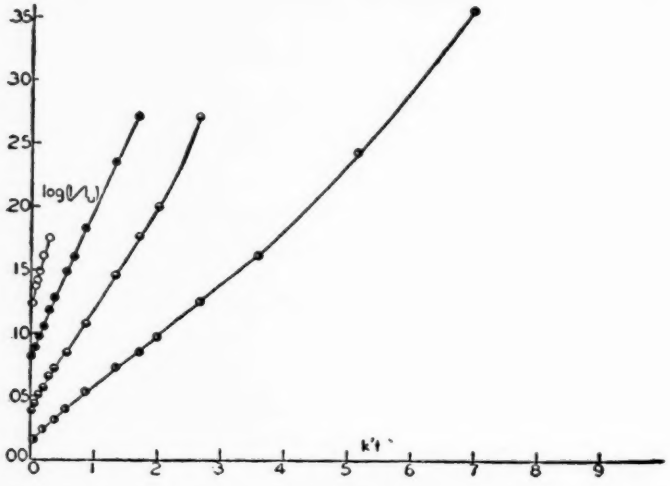


FIG. 6.—Creep curves of H-11 at 60° C l = extended length at time t, l_u = unextended length, l_0 = initial extended length: k' = rate constant obtained from stress relaxation data at 60° C. Log_{10} vs. $k't$, ○ l_0 = 32.8 per cent, ● l_0 = 20.8 per cent, ◒ l_0 = 9.4 per cent, ◑ l_0 = 3.2 per cent.

Observations were also made on the mechanical behavior after removal of load during creep experiments. An initial rapid contraction followed by a small, slow creep recovery was noticed. If we had a system that could be strictly characterized by one reaction rate, as in Equation (2), we could expect no creep recovery. Actually about 5 per cent recovery is observed, which is not surprising in view of the slight deviation from $e^{-k't}$ evinced in Figure 4.

The theory previously derived, which apparently explains satisfactorily the creep of Butyl and Hevea rubbers at elevated temperatures is strictly true only in the case that there is only a scission reaction. The satisfactory agreement for Butyl and Hevea occurs because in these rubbers the scission reaction predominates. This theory does not apply, nor can it be expected to apply to polysulfide rubbers, where the rate of bond formation in the network structure is equal to the rate of bond breaking.

TABLE I

64H	H3	H5	H8	H9	H10	H11	H12
Organic tetrasulfide	100	—	—	—	—	—	—
Organic tetrasulfide	—	100	—	—	—	—	—
Organic disulfide cross-linked	—	—	100	—	—	—	—
Organic disulfide	—	—	—	100	—	—	—
Organic disulfide tetrafunctional	—	—	—	—	100	—	—
Organic disulfide	—	—	—	—	—	100	—
Organic disulfide with 40% monosulfide	—	—	—	—	—	—	100
Zinc oxide	10	10	—	—	—	10	—
Pelletex	—	60	60	60	60	60	60
Micronex	25	—	—	—	—	—	—
Stearic acid	.50	.50	.50	1.00	1.00	.50	1.00
Benzothiazyl disulfide	—	—	—	—	—	.30	—
Diphenylguanidine	.10	—	—	—	—	.10	—
Tetramethylthiuram disulfide	.25	.25	—	—	—	—	—
Lead peroxide	—	—	1.50	1.50	1.50	—	1.50
Cure	50×287	30×287	30×287	30×287	30×287	50×298	30×287
Modulus 100%	—	—	540	310	450	515	340
300%	—	—	—	1200	1475	1185	—
500%	—	—	—	—	—	—	—
Tensile strength (lbs. per sq. in.)	730	450	1160	1520	1475	1185	985
Elongation (percentage)	370	400	190	420	300	300	280
Set (percentage)	—	—	2	5	3	10	5
Hardness	74	70	73	68	74	76	64

RELAXATION STUDIES OF VARIOUS POLYSULFIDE RUBBERS OVER A RANGE OF TEMPERATURE

To obtain further insight into the nature of bonds whose rupture is responsible for the relaxation of stress in polysulfide rubbers, a series of these rubbers prepared for us by the Thiokol Company were studied over a range of temperatures. The rubbers studied included two tetrasulfide polymers H-3 and H-5, two linear disulfides, a disulfide containing a fairly large percentage of monosulfide linkages, one disulfide containing two per cent of trifunctional agent, and one disulfide containing one per cent of tetrafunctional agent. Table I

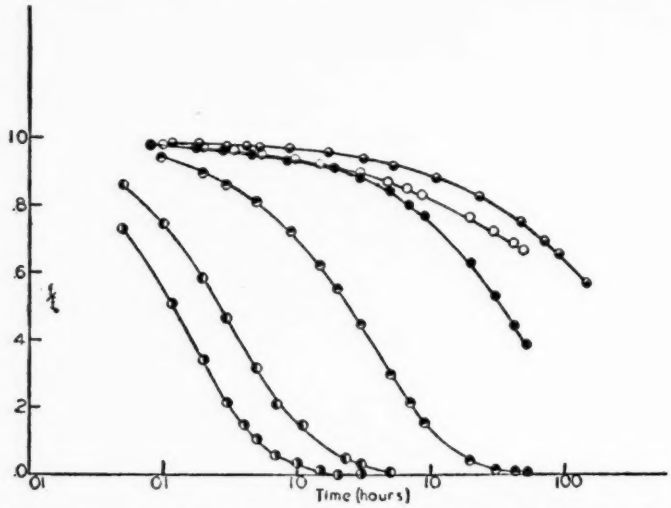


FIG. 7.—Continuous stress relaxation of various polysulfide rubbers at 60° C, 50 per cent elongation. ◒ H-10, ○ H-2, ● H-7, ◓ H-11, ◐ H-3, ◑ H-5. (See Table I.)

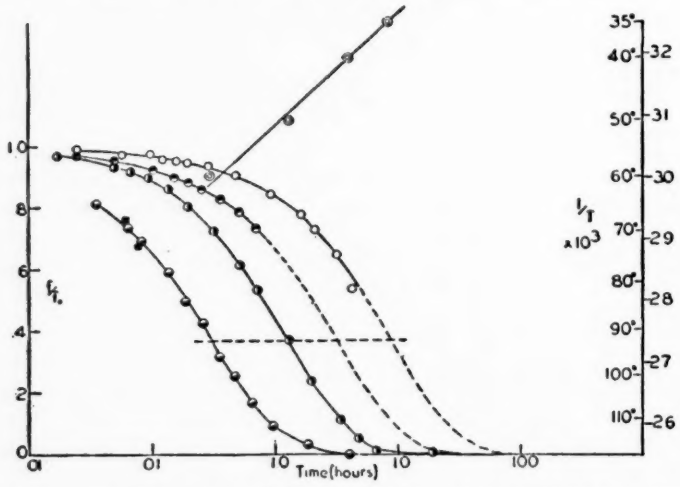


FIG. 8.—Continuous stress relaxation of H-3 at various temperatures and 50 per cent elongation: plot of log k' *vs.* $1/T$. ○ 35° C, ◓ 40° C, ◑ 50° C, ◒ 60° C.

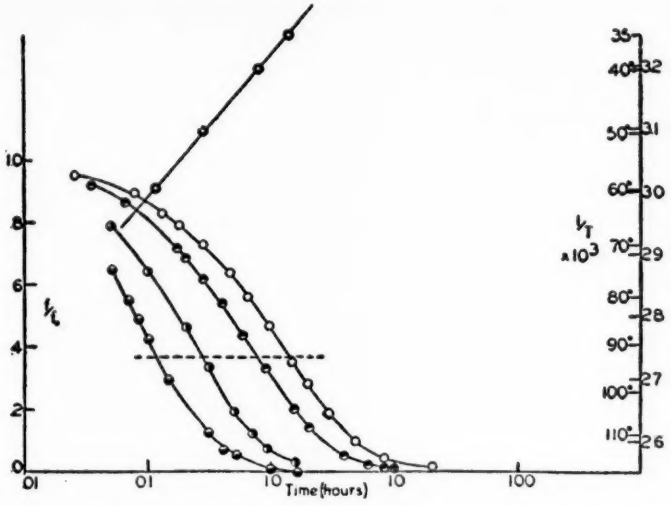


FIG. 9.—Continuous stress relaxation of H-5 at various temperatures and 50 per cent elongation; plot of log k' *vs.* $1/T$. ○ 35° C, ◓ 40° C, ◑ 50° C, ◒ 60° C.

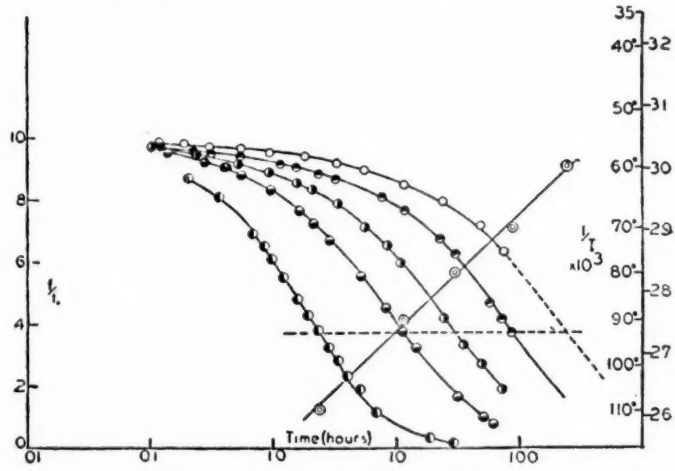


FIG. 10.—Continuous stress relaxation of H-8 at various temperatures and 50 per cent elongation; plot of log k' *vs.* $1/T$. ○ 60° C, ◓ 70° C, ◑ 80° C, ◒ 90° C, ◐ 110° C.

details these polymers and the compounding and curing recipe for the rubbers obtained therefrom. The relaxation curves for all these rubbers at 60° C is shown in Figure 7. It is evident that the relaxation rate varies by a factor of about one thousand from the fastest to the slowest of these compounds. The tetrasulfides relax the most rapidly; the inclusion of polyfunctional agents apparently slightly retards the rate of relaxation.

The temperature dependence of the relaxation rates for these rubbers is shown in Figures 8 to 14. In these graphs, stress divided by initial stress is plotted against logarithmic time for a series of different temperatures. Inas-

much as all the decay curves are approximated by the decay law $e^{-k't}$, a very simple method for obtaining the activation energies for stress decay was employed. As shown in Figure 8, a horizontal line was drawn across the graphs at a value of $f/f_0 = .368 = 1/e$. The intersection of this horizontal line with the decay curves at the various temperatures gives the time for which $k' = 1/t$.

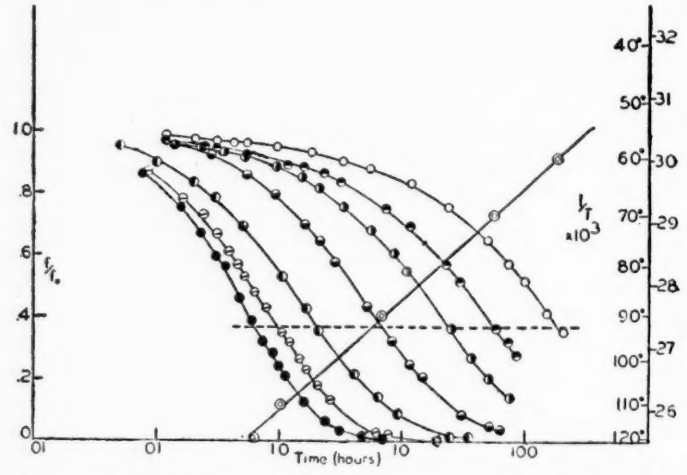


FIG. 11.—Continuous stress relaxation of H-9 at various temperatures and 50 per cent elongation; plot of log k' *vs.* $1/T$. ○ 60° C, ◓ 70° C, ◑ 80° C, ◒ 90° C, ◐ 100° C, ⊖ 110° C, ● 120° C.

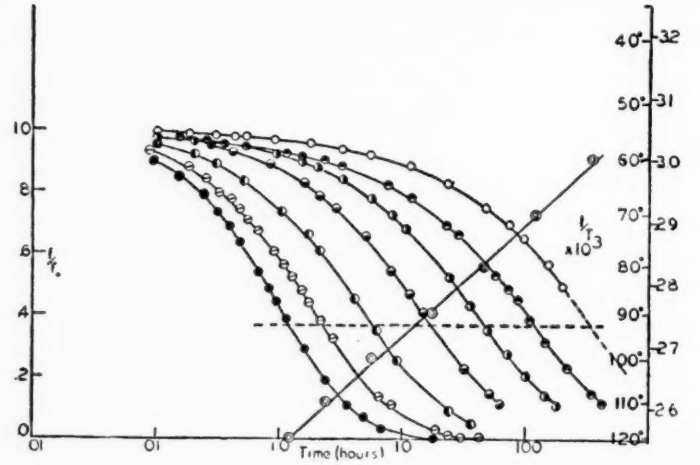


FIG. 12.—Continuous stress relaxation of H-10 at various temperatures and 50 per cent elongation; plot of log k' *vs.* $1/T$. ○ 60° C, ◓ 70° C, ◑ 80° C, ◒ 90° C, ◐ 100° C, ⊖ 110° C, ● 120° C.

Since in these curves time is already plotted on a logarithmic scale, a scale of reciprocal absolute temperature is plotted on the right-hand side of the figures along the ordinate scale. By locating the time for which $t = 1/k'$ against the corresponding temperature on the reciprocal temperature scale, a plot of log $1/k'$ *vs.* $1/T$ is obtained. The figures indicate that straight lines are obtained

for all the rubbers studied, and the slopes of the straight lines give a measure of the heat of activation. The heats of activation for the various rubbers are tabulated in Table II, as are the entropies of activation. It is clear that, although the absolute values of the relaxation rates are very different (see Figure 7), the heats of activation for all the polysulfide rubbers do not differ markedly.

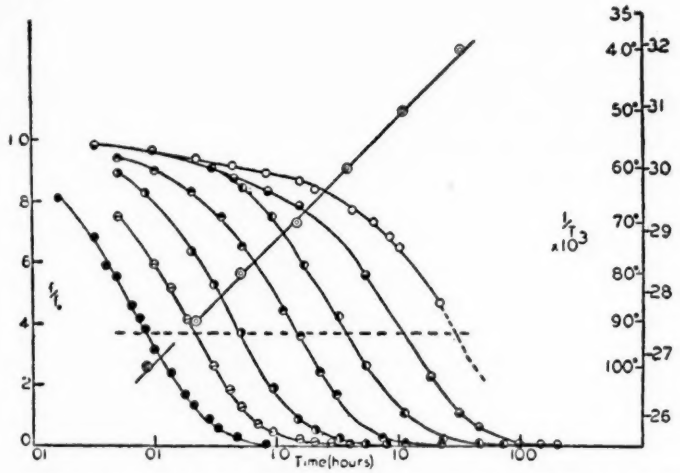


FIG. 13.—Continuous stress relaxation of H-11 at various temperatures and 50 per cent elongation; plot of log k' *vs.* $1/T$. ○ 40° C, ◒ 50° C, ◐ 60° C, ◓ 70° C, ◑ 80° C, ⊖ 90° C, ● 100° C.

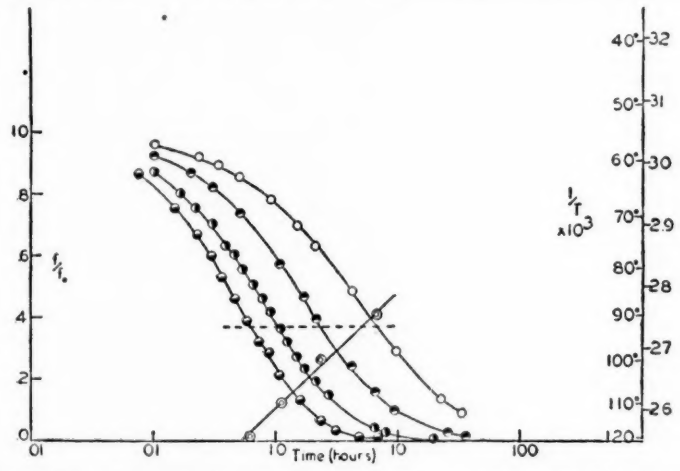


FIG. 14.—Continuous stress relaxation of H-12 at various temperatures and 50 per cent elongation; plot of log k' *vs.* $1/T$. ○ 90° C, ◓ 100° C, ◑ 110° C, ◒ 120° C.

A pair of curves suffices to present the complete stress-time-temperature relations for a given rubber. For example, Figure 15 shows how this can be done for H-11. A "universal stress-decay curve" is plotted against log $k't$ inasmuch as the decay curves are approximately superposable by translation along the logarithmic time axis. A plot of log k' against $1/T$ is shown on the

TABLE II

Polymer	$\Delta H^{\ddagger}$ (kcal.)	$\Delta S^{\ddagger}$ (cal.)
H-3	25.41	+3.3
H-5	20.24	−10.0
H-8	24.28	−13.1
H-9	25.70	−8.2
H-10	25.08	−11.5
H-11	22.92	−8.9
H-12	24.47	−11.5

same figure, where the same logarithmic scale is used as abscissa and the $1/T$ scale is plotted as the ordinate scale on the right-hand side of the figure. The values of k' at any temperature for this graph can be readily obtained from Figure 13 by taking the reciprocal of the time at the given temperature at which the value of $f/f_0 = e^{-1}$. Figure 15 may now be used to give the complete

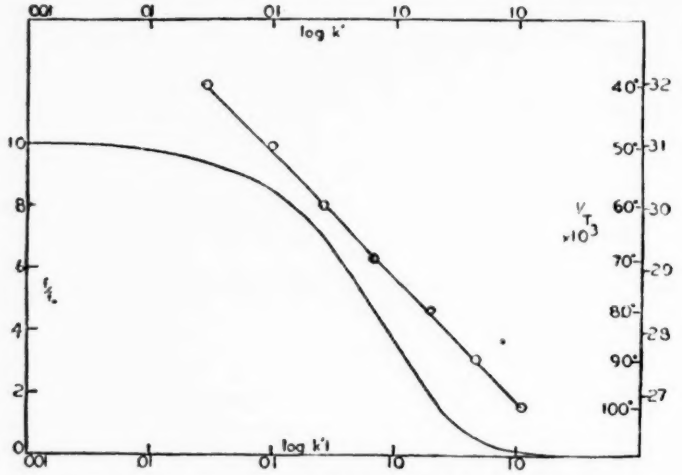


FIG. 15.—"Universal curve" of H-11 and plot of log k' *vs.* $1/T$.

stress-time behavior for relaxation at any temperature. The log-time scale at any temperature always has the spacing shown along the abscissa, and may be located along the abscissa by using the straight-line locus of log k' *vs.* $1/T$.

DISCUSSION

The simple relaxation behavior (given by Equation (2)) of any single polysulfide rubber studied here is strong evidence that a single type of bond in the structure is involved. Furthermore, the approximate equality of the energy of activation for stress decay in all the polysulfide rubbers is an indication that the relaxing bond is in each case closely similar, perhaps identical, even in the case of the disulfides and tetrasulfides. Moreover, the facts indicate that the total number of structural elements does not change with time or temperature, so that the bonds involved reform at exactly the same rate that they break, and the equilibrium between breaking and reforming of bonds does not change with temperature.

It is not possible to make a final decision at this point as to precisely which bond of the structure is responsible for relaxation. It is conceivable that a

primary chemical bond along the chain is breaking and reforming, possibly by the simple expedient of bond interchange between two chains. On the other hand, it is also possible that the cross-linking bond between chains is in fact responsible for the thermoplastic behavior. It was hoped that the use of tetrafunctional and trifunctional cross-linking agents would provide a means of tying the molecules into a three-dimensional structure. If these cross-linked polymers showed a limited relaxation instead of a complete relaxation to zero stress, it would be possible to state unequivocally that the relaxation in the linear disulfides and tetrasulfides was due to a slippage of interchain bonds. On the other hand, there is no conclusive evidence that the tetra and trifunctional agents used actually produce three-dimensional structures.

Considerations of the various possibilities put reasonable limits to the types of bonds responsible for polysulfide behavior. There are at least three bonds along the network chains, any one of which may be responsible for the observed

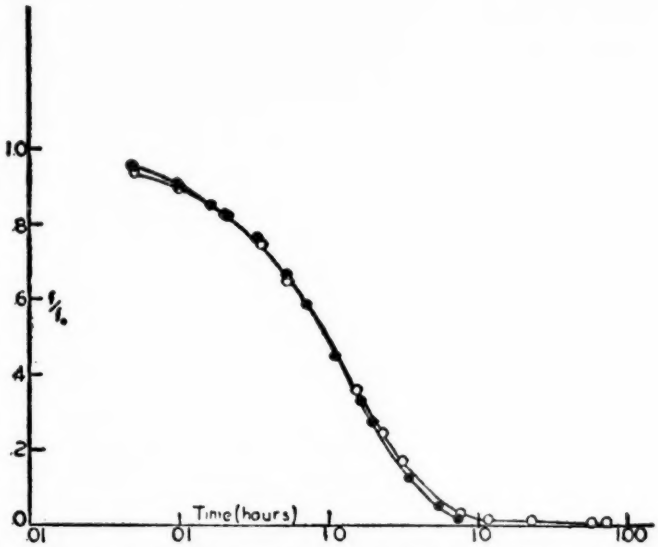


FIG. 16.—Continuous stress relaxation of H-11 in vacuum and air at 70° C, 50 per cent elongation. ○ Air, ● Vacuum.

phenomena. Whatever the bond, it must: (1) have a low activation energy; (2) be formed as rapidly as it is broken throughout the temperature range, 35°–120° C, and (3) be insensitive to whether it is heated in vacuum or air. The three bonds along the polysulfide network chains are the C—C, C—S, and S—S bonds. Pauling[4] gives the C—C bond energy (per mole) as 58.6 kcal., the C—S as 54.5 kcal., and the S—S bond energy as 63.8 kcal. The C—S bond thus appears to be the weakest and the S—S bond the strongest of the three.

The experiments on creep in vacuum and stress relaxation in oxygen-free nitrogen indicate that the relaxation behaviors of the hydrocarbon rubbers are due to oxidative attack, since the rate of scission is decreased a thousandfold in vacuum at 10^{-5} mm. pressure[5]. Experiments on relaxation of polysulfide rubbers in vacuum at 10^{-5} mm. pressure indicate that oxygen is not responsible

for their relaxation behavior (Figure 16). On the other hand, temperature does appear to have a primary effect on the relaxation rates of polysulfides both in vacuum and air as contrasted to its secondary effect on hydrocarbon rubbers in vacuum[5]. Furthermore, the ΔH^* of hydrocarbon rubbers of 30.4 $\pm$2.0 kcal., contrasted to the ΔH^* of 24 $\pm$ 1.5 kcal. in polysulfides, indicates that essentially one type of chemical reaction involving very similar chemical bonds is responsible for the relaxation behavior of all the hydrocarbon rubbers and that this reaction is not the same as the one responsible for polysulfide behavior. Thus it appears reasonable to assume that the hydrocarbon portion of the structure is not responsible for polysulfide behavior, although the possibility does exist that a C—C bond adjacent to a sulfur atom in a network chain may be sufficiently weakened by the presence of the sulfur atom to satisfy the conditions stated above. The accessibility of *d*-orbitals in sulfur to partial double-bond formation makes such a weakening of adjacent C—C bonds possible, and poses a problem for further research.

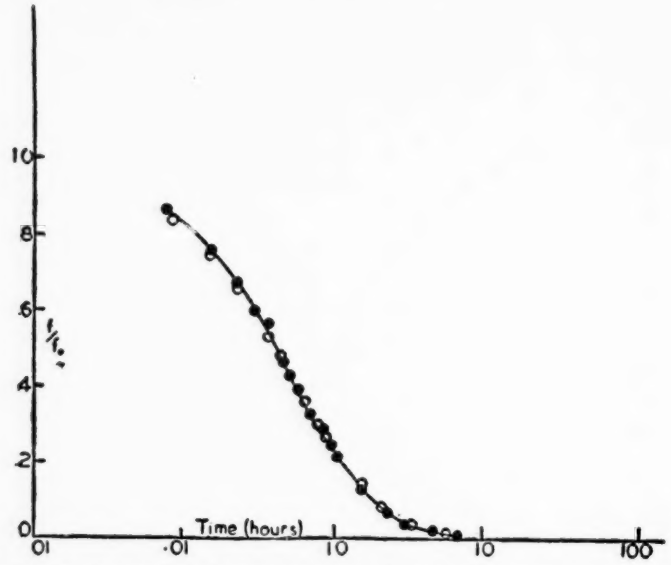


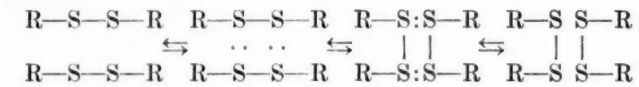
FIG. 17.—Continuous stress relaxation of H-9 and H-12 at 120° C, 50 per cent elongation. ● H-9 (disulfide), ○ H-12 (monosulfide and disulfide).

The relaxation experiments on H-12, a rubber consisting of both monosulfide and disulfide links along the network chains, indicate that there is little difference in its relaxation rate from that of a disulfide polymer (Figure 17). The fact that there is little difference in the relaxation rates of the two rubbers indicates that the C—S bond is at least as strong, if not stronger, than the S—S bond. Furthermore, as pointed out in Gilman[6], the formation of monosulfides (the C—S bond) from mercaptans occurs at high temperatures in the presence of catalysts such as metallic sulfides; the hydrogen attached to the α-carbon in monosulfides is more acidic than in corresponding ethers (pointing up the tendency of sulfur to expand its valence shell due to the accessibility of its *d*-orbitals, producing partial double bonds[7], thus strengthening the C—S bond and weakening the C—H bond on the α-carbon); organic monosulfides do not

react readily with elementary sulfur to form higher sulfides, whereas disulfides, trisulfides, and tetrasulfides readily add sulfur to form higher sulfides; conversely di- and trisulfides may also be readily formed from higher sulfides by distillation. All these facts indicate that the S—S bond is more labile and less stable than the C—S bond, in contrast to their respective bond energies as given by Pauling. A further instance of this is provided by Powell and Eyring[8], who have indicated an S—S bond energy of 27.5 ± 5 kcal., compared with the Pauling value of 63.8 kcal.

In addition to bond scission along the primary valence chains of the polysulfide rubbers, it is also possible that relaxation is due to a slippage or rupture of bond between the polysulfide chains. It is not known at present whether the vulcanization process introduces primary cross-links into the structure, and, if so, what the nature or energy of these cross bonds might be. It is conceivable that cross-linking in these rubbers is not due to the vulcanization process but instead occurs through formation of relatively strong bonds between sulfur atoms in adjacent chains. These bonds, which may possibly involve the unshared electron in the sulfur valence shell, would be stronger than ordinary secondary bonds between chains, but weaker than most primary chemical bonds. The relaxation process may consist in the breaking and reformation of these interchain bonds.

The relaxation may also occur by a process of chain interchange to give two new chains which are chemically indistinguishable from the old ones and from each other. Such a process of chain interchange is illustrated below for the case of the disulfide linkage:



A mechanism of this or similar type would account for all of our observed phenomena.

A final possibility exists, namely, that some chemical agent introduced into the rubber in the emulsion or during compounding may be involved in breaking the polysulfide chains.

It is evident that complete identification of the bond responsible for relaxation in polysulfide rubbers would be of great interest, and that this identification will accompany an enhanced knowledge of the chemistry of mono- and polysulfides.

SUMMARY

Polysulfide rubbers of various internal structures have been investigated by measurements of continuous and intermittent relaxation of stress and by creep under constant load at temperatures between 35° C and 120° C. Continuous stress relaxation measurements indicate that these rubbers obey approximately the simple Maxwellian law of relaxation of stress, which indicates that one definite type of bond in the network structure is responsible for stress decay. The activation energy for the relaxation process in each of the polysulfide rubbers is nearly the same, indicating that the same type of bond is responsible for the relaxation behavior of all the polysulfides investigated. In contrast to hydrocarbon rubbers, oxygen is not the cause of high temperature relaxation in polysulfide rubbers, nor does heating in air at moderate temperatures for times comparable to the relaxation time produce changes in

physical properties as determined by modulus or by appearance of the samples. Several possibilities regarding the mechanism of the relaxation process and the type of bond involved are considered in the light of the experimental results.

ACKNOWLEDGMENTS

The authors wish to thank the Firestone Tire and Rubber Company and Princeton University for making possible our researches on the fundamental properties of high polymeric materials, and the Thiokol Corporation for contributing the Thiokol samples which made this particular investigation possible. In particular, we wish to thank J. C. Patrick, F. O. Davis, and E. Fettes of the Thiokol Corporation, and M. Mochulsky of Princeton, for the coöperation and useful advice they have rendered us.

REFERENCES

[1] Tobolsky, Prettyman and Dillon, *J. Applied Physics* **15**, 380 (1944); Tobolsky and Andrews, *J. Chem. Phys.* **13**, 3 (1945).
[2] Wall, *J. Chem. Phys.* **10**, 132, 485 (1942); Guth and James, *J. Chem. Phys.* **11**, 455 (1943); Treloar, *Trans. Faraday Soc.* **40**, 59 (1944); Flory, *Chem. Rev.* **35**, 51 (1944).
[3] Andrews, Mesrobian and Tobolsky, *Trans. Am. Soc. Mech. Eng.* **67**, 569 (1945).
[4] Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N. Y., **1939.**
[5] Unpublished experiments of W. C. Scheider and M. Magat, and also unpublished work of the present authors.
[6] Gilman, "Organic Chemistry", John Wiley & Sons, New York, Vol. 1, p. 853.
[7] Rothstein, *J. Chem. Soc.* **1940**, pp. 1550, 1553, 1558, 1560.
[8] Powell and Eyring, *J. Am. Chem. Soc.* **65**, 648 (1943).

INDEX

RUBBER CHEMISTRY AND TECHNOLOGY VOLUME XIX, 1946

AUTHOR INDEX

Page

ABADIE, PAUL. *See* GIRARD, PIERRE.
ALEKSANDROV, A. P. AND LAZURKIN, J. S. Strength of amorphous and of crystallizing rubberlike polymers 42
ALFREY, TURNER, HENDRICKS, J. G., HERSHEY, ROBERT M. AND MARK, HERMANN. Nonsulfur vulcanization. II. An experimental study 652
ALTMAN, R. F. A. Organic analysis of Hevea latex. VII. Fat acids, resin acids, sterols, and wax-alcohols. A preliminary note 788
Organic analysis of Hevea latex. VIII. Development of a general scheme of analysis 781
ANDREWS, R. D., TOBOLSKY, A. V. AND HANSON, E. E. Theory of permanent set at elevated temperatures in natural and synthetic rubber vulcanizates 1099
ANDRÉ, ROUX. *See* LAINÉ, P.
ANTHONY, ROBERT L. *See* GUTH, EUGENE; HAMILL, W. H.

BATEMAN, L. Photochemical breakdown of rubber 283
——— AND JEFFREY, G. A. Structure of polyisoprenes. IV. Double-bond interaction in certain carbalkoxy-substituted 1,5-dienes 14
———AND KOCH, H. P. Structure of polyisoprenes. V. Ultraviolet absorption spectra of certain carbalkoxy-substituted 1,5-dienes and the charge-resonance spectra of glutaconic ester enolate ions 23
BEKKEDAHL, NORMAN. *See* WOOD, LAWRENCE A.
BHATNAGAR, S. S., KARIMULLAH AND SHANKAR, UMA. Extraction of rubber from Cryptostegia grandiflora 193
BLOOMFIELD, GEORGE F. Rubber, polyisoprenes and allied compounds. VIII. Formation of dialkyl sulfide dihalides, and its bearing on the problem of determining the unsaturation of vulcanized rubber 287
BLOXHAM, J. L. *See* PARKINSON, D.
BOLLAND, J. L. AND ORR, W. J. C. Thermal breakdown of rubber 277
BONNET, (Miss) ODETTE. *See* COMPAGNON, PATRICE.
BUCHAN, S. AND RAE, W. D. Chemical nature of the rubber-to-brass bond 968
Physical examination of brass deposits .. 208
——— AND SHANKS, J. R. Study of the rubber-metal bond 956
BUCKINGHAM, R. AND PLANER, G. V. Gelation of rubber sols by ultraviolet light. Photogelation of rubber sols in the absence of accelerators 632
BUIST, J. M. Using the Mooney viscometer. 645
——— AND WELDING, G. N. Use and misuse of accelerated aging tests 821
BULGIN, D. Electrically conductive rubber. 444
BURCHFIELD, H. P. Qualitative spot tests for rubber polymers 667
832

Page

BUSSE, W. F., LAMBERT, J. M. AND VERDERY, R. B. Tackiness of GR-S and other elastomers 1163

CHEYNEY, LA VERNE E. *See* KECK, MAX H.
CHOVIN, P. Proöxygenic effect and the resulting deterioration of rubber 296
CHURCH, H. F. AND DAYNES, H. A. Properties of hard rubber. XV. Influence of rubber-sulfur ratio and vulcanization time on the properties of pure rubber-sulfur compositions. (1) Chemical composition, density, and thermal expansion 760
———, COOPER, L. H. N. AND DAYNES, H. A. Properties of hard rubber, XIV. Influence of some ingredients on surface deterioration in sunlight 753
COMPAGNON, PATRICE. *See* DUFRAISSE, CHARLES. Anhydride rubber. II. Production and vulcanization 319
COTTON-FEYTIS, EUGENIE. Magnetic anisotropy of rubber 349
CRABTREE, JAMES AND KEMP, A. R. Weathering of soft vulcanized rubber 712
CRAGG, L. H. Terminology of intrinsic viscosity and related functions 1092
COMPTON, JACK. *See* LESSIG, E. T.
CONRAD, CARL M. *See* PHILIPP, HOWARD J.
COOPER, L. H. N. *See* CHURCH, H. F.

DAVIES, B. L. Accelerated vulcanization of ebonite 948
DAYNES, H. A. *See* CHURCH, H. F.
DILLON, J. H. AND PRETTYMAN, I. B. Effects of temperature and humidity on the physical properties of tire cords 233
DUFRAISSE, CHARLES AND COMPAGNON, PATRICE. Principles of method of vulcanization based on condensation reactions. Prosthesis and synesis 329
——— AND HOUPILLART, JEAN. Applications of ultraviolet spectrography. Study of some accelerators 1051
DUFOUR, RENÉ. *See* LEDUC, HENRI.

ESKEW, RODERICK K. Natural rubber from Russian dandelion 856

FARMER, E. H. Oxidative breakdown of rubber 267
——— AND SUTTON, DONALD A. Course of autoöxidation reactions in polyisoprenes and allied compounds. XI. Double-bond movement during the autoöxidation of a monoölefin 1022
FERRY, (Miss) J., GEE, GEOFFREY AND TRELOAR, L. R. G. Interaction between rubber and liquids. VII. Heats and entropies of dilution of natural rubber by various liquids 1
FIELD, J. E., WOODFORD, D. E. AND GEHMAN, S. D. Applications of infrared methods in the structural examination of synthetic rubber 1113

Page

FLETCHER, W. P. *See* MOYAL, J. E.
FLORY, PAUL J. Effects of molecular structure on physical properties of Butyl rubber 552
Tensile strength in relation to molecular weight of high polymers 559
FOURNIER, HENRI AND THILLAT, JEAN-JACQUES. x-Ray studies of synthetic rubbers. Polychloroprene 1088

GEE, GEOFFREY. *See* FERRY, (Miss) J.
GEHMAN, S. D. *See* FIELD, J. E.
GIBSON, RALPH A. *See* WOOD, LAWRENCE A.
GIRARD, PIERRE AND ABADIE, PAUL. Hertzian spectrum of rubber and its micellar structure 1085
GOLDFINGER, GEORGE. Mechanism of reënforcement. II 616
GOPPEL, J. M. AND VAN ROSSEM, A. x-Ray investigation of the calender effect in rubber sheets 403
GOUGH, V. E. *See* POWELL, E. F.
GRAVES, F. L. Improved brittle-point apparatus 844
GURNEY, W. A. Adhesion of rubber to brass plate 199
GUTH, EUGENE, WACK, PAUL E. AND ANTHONY, ROBERT L. Significance of the equation of state for rubber 1137

HAEGEL, JEAN. Mobility of foreign molecules dissolved in rubber 987
HAEHL, A. Effects of proöxygenic substances on reclaimed rubber 123
——— AND LE BRAS, JEAN. Influence of milling on the plasticization of rubber 938
HAMILL, W. H., MROWCA, B. A. AND ANTHONY, R. L. Specific heats of Hevea, GR-S and GR-I stocks 622
HANSON, E. E. *See* ANDREWS, R. D.
HAUSER, ERNST A. Morphology of rubber latex particles 187
———, LE BEAU, D. S. AND SHEN, YEN. Study of the various molecular fractions of rubber and their behavior during vulcanization 502
HAVENHILL, R. S., O'BRIEN, H. C. AND RANKIN, J. J. Electrostatic and tensile properties of rubber and GR-S at elevated temperatures 428
HENDRICKS, S. B., WILDMAN, S. G. AND JONES, E. J. Differentiation of rubber and gutta hydrocarbons in plant materials 501
HERINGTON, E. F. G. Study of the mechanism of polymerization reactions by means of size-distribution curves 36
HERSHEY, ROBERT M. *See* ALFREY, TURNER.
HESSELS, J. H. E. State of polydispersion of Hevea latex 176
HOLLISTER, JOSEPH. *See* MORRIS, ROSS E.
HOUPILLART, JEAN. *See* DUFRAISSE, CHARLES.
HUBLIN, ROGER A. Capacity of rubber mixtures to be moulded 466
New method for determining the filler content of vulcanized rubber 482
HUGGINS, MAURICE L. New approach to the theory of rubberlike elasticity 511

JARRIJON, ANDRÉ. Application of ultraviolet spectrography. Study of the transformation which tetramethylthiuram disulfide undergoes during the process of vulcanization 1061
Hardening of crude rubber 400
JEFFREY, G. A. Structure of polyisoprenes. I. Crystal structure of geranylamine hydrochloride 351
——— *See* BATEMAN, L.
JONES, E. J. *See* HENDRICKS, S. B.

KARIMULLAH. *See* BHATNAGAR, S. S.
KECK, MAX H. AND CHEYNEY, LA VERNE E. Structural changes in vulcanization of Buna-S 534
KEMP, A. R. *See* CRABTREE, JAMES.
KOCH, H. P. *See* BATEMAN, L.
KONINGSBERGER, C. AND SALOMON, G. Preparation and properties of rubberlike high polymers. I. Polymerization of dienes and vinyl compounds in bulk 1029

LAINÉ, PAUL AND ROUX, ANDRÉ. Hardness tests at low temperatures 933
LAMBERT, J. M. *See* BUSSE, W. F.
LAZURKIN, J. S. *See* ALEKSANDROV, A. P.
LE BEAU, D. S. *See* HAUSER, ERNST A.
LE BRAS, JEAN. A new material: anhydride rubber. I 313
Influence of vulcanization on the oxidizability of rubber. II. Vulcanizing agents other than sulfur 876
——— *See* HAEHL, A.
LEDUC, HENRI AND DUFOUR, RENÉ. Concentration of latex by means of electric currents of high frequency 486
LESSIG, E. T. AND COMPTON, JACK. Single-cord compression adhesion test for evaluating the adhesion of vulcanized rubber to cord 223
LONDON ADVISORY COMMITTEE FOR RUBBER RESEARCH. Report of conference on post-war preparation and packing of rubber ... 865

MALLARD, PAUL A. *See* MORRIS, ROSS E.
MARK, HERMANN. *See* ALFREY, TURNER.
MARTIN, GEORGE. Relation between the quality of latex and its chemical composition 494
MEEHAN, E. J. Spectrophotometric determination of styrene content of butadiene-styrene copolymers 1077
MEYER, KURT H. AND VAN DER WYK, A. J. A. Molecular processes during the deformation of rubberlike elastic bodies 525
MORRIS, ROSS E., HOLLISTER, JOSEPH AND MALLARD, PAUL A. Cold-compression sets of natural and synthetic vulcanizates. 151
MOYAL, J. E. AND FLETCHER, W. P. Free and forced vibration methods in the measurement of the dynamic properties of rubbers 163
MROWCA, B. A. *See* HAMILL, W. H.
MULLINS, L. Evaluation of physical properties of rubber vulcanizates at low temperatures 915

NAYLOR, RALPH F. Behavior of ketene towards olefins and olefinic peroxides. 63
Reactivity of isoprenic and analogous hydrocarbons towards thiocyanic acid and dithiocyanogen 34

O'BRIEN, H. C. *See* HAVENHILL, R. S.
ORR, W. J. C. *See* BOLLAND, J. L.

PARKINSON, D. Carbon blacks in GR-S 100
——— AND BLOXHAM, J. L. Behavior of natural rubber and GR-S under repeated stress cycles 417
PEAKER, C. R. Procedure for determining physical properties of films from GR-S latices 190
PETROVA, A. *See* TSVETKOV, V. N.
PHILIPP, HOWARD J. AND CONRAD, CARL M. Control of elongation in highly stretched cotton tire cord 253
PIPER, G. H. AND SCOTT, J. R. Rubber plastometer with uniform rate of shear. Shearing-cone plastometer 822
PLANER, G. V. *See* BUCKINGHAM, R.
POWELL, E. F. AND GOUGH, V. E. Mechanism of rubber cracking 406
PRETTYMAN, I. B. *See* DILLON, J. H.

RAE, W. D. *See* BUCHAN, S.
RANKIN, J. J. *See* HAVENHILL, R. S.
REHNER, JOHN, JR. Elastic deformation and molecular weight in polystyrene 1047
——— AND FLORY, PAUL J. Vulcanization reactions in Butyl rubber Action of dinitroso, dioxime and related compounds .. 900

Page

REITLINGER, S. A. Gas permeability and the microstructure of polymers..... 385
RUSH, IAN C. Effect of moisture on GR-S. Rate of cure and physical properties..... 773

SALOMON, G. *See* KONINGSBERGER, C.
SCOTT, J. R. Methods of calculating and representing rheological properties, using data from the parallel-plate plastometer.. 461
Shellac as an ingredient of rubber compositions..... 125
——— *See* PIPER, G. H.
SEIFRIZ, WILLIAM. Coagulation of latex.... 491
SHANKAR, UMA. *See* BHATNAGAR, S. S.
SHANKS, J. R. *See* BUCHAN, S.
SHELTON, J. REID AND WINN, HUGH. Oxidation of GR-S vulcanizates..... 696
SHEN, YEN. *See* HAUSER, ERNST A.
SHEPPARD, N. AND SUTHERLAND, G. B. B. M. Some infrared studies on the vulcanization of rubber..... 66
SOCIÉTÉ DES MATIÈRES COLORANTES ET PRODUITS CHIMIQUES DE SAINT-DENIS, FRANCE. Measurement of the plasticity of Buna-S with the Williams apparatus.. 478
STERN, M. D. AND TOBOLSKY, A. V. Stress-time-temperature relations in polysulfide rubbers..... 1178
STEVENS, HENRY P. Rubber photogelling agents. II..... 394
SUTHERLAND, G. B. B. M. *See* SHEPPARD, N.
SUTTON, DONALD A. *See* FARMER, E. H.

TAYLOR, ROLLA H. Factors affecting results obtained with the Mooney viscometer.... 808
——— T. M. Cooling facilities of rubber equipment..... 218
TERTIAN, ROBERT. *See* TRILLAT, JEAN-JACQUES.
THOMPSON, H. W. AND TORKINGTON, P. Infrared spectra of compounds of high molecular weight..... 46
TOBOLSKY, A. V. *See* ANDREWS, R. D.; STERN, M. D.
TORKINGTON, P. *See* THOMPSON, H. W.
TRELOAR, L. R. G. Elasticity of a network of long-chain molecules. III..... 1009

Page

Statistical length of long-chain molecules. 1002
——— *See* FERRY, (Miss) J.
TRILLAT, JEAN-JACQUES. Study of rubb-sulfur mixtures by radiomicrography.... 392
——— *See* FOURNIER, HENRI.
——— AND TERTIAN, ROBERT. Structure of synthetic rubbers. Ethylene polysulfide. 1090
TSVETKOV, V. N. AND PETROVA, A. Nature of dynamic double refraction in rubber solutions, and the shape of rubber molecules... 360

VAN AMERONGEN, G. J. Modified method for the direct estimation of the absorption of oxygen by rubber..... 170
VAN DER BIE, G. J. Comparison of different types of rubber obtained from the same field latex..... 848
VAN DER WYK. *See* MEYER, KURT H.
VAN ROSSEM, A. *See* GOPPEL, J. M.
VERDERY, R. B. *See* BUSSE, W. F.

WACK, PAUL E. *See* GUTH, EUGENE.
WAKE, W. C. Recent advances in rubber analysis..... 792
WALL, FREDERICK T. AND ZELIKOFF, MURRAY. Surface film thicknesses of polymeric substances in relation to molecular structure..... 551
WELDING, G. N. *See* BUIST, J. M.
WILDMAN, S. G. *See* HENDRICKS, S. B.
WILDSCHUT, A. J. Proportion of crystalline and amorphous components in stretched vulcanized rubber..... 86
WINN, HUGH. *See* SHELTON, J. REID.
WOOD, LAWRENCE A. AND BEKKEDAHL, NORMAN. Crystallization of unvulcanized rubber at different temperatures..... 1145
———, BEKKEDAHL, NORMAN AND GIBSON, RALPH A. Effect of pressure on the melting of crystalline rubber..... 546
WOODFORD, D. E. *See* FIELD, J. E.

ZELIKOFF, MURRAY. *See* WALL, FREDERICK T.

SUBJECT INDEX

Absorption of oxygen by rubber..... 170
Accelerators, study of some..... 1051
Accelerated vulcanization of ebonite..... 948
Adhesion, compression, test..... 223
of rubber to brass plate..... 199
Aging, accelerated, tests..... 444
Amorphous components in stretched vulcanized rubber..... 1124
rubberlike polymers, strength of..... 42
Analysis, organic, of Hevea latex..... 781
rubber, recent advances in..... 792
Anhydride rubber. I..... 313
II. Production and vulcanization..... 319
Anisotropy, magnetic..... 349
Apparatus, improved brittle point..... 844
Application of ultraviolet spectrography. Study of the transformation which tetramethylthiuram disulfide undergoes during the process of vulcanization..... 1061
Applications of infrared methods in the structural examination of synthetic rubber... 1113
of ultraviolet spectrography. Study of some accelerators..... 1051
Autoöxidation reactions in polyisoprenes.... 1022

Behavior of ketene towards olefins and olefinic peroxides..... 63
of natural rubber and GR-S under repeated stress cycles..... 417
Brass deposits, physical examination of..... 208
plate, adhesion of rubber to..... 199
rubber-to-, bond..... 968
Breakdown of rubber, oxidative..... 267
photochemical..... 283
thermal..... 277
Brittle-point apparatus..... 844
Buna-S, structural changes in vulcanization of 534
Butadiene-styrene copolymers..... 1077
Butyl rubber, effects of molecular structure on physical properties of..... 552
vulcanization reactions in..... 900

Calendar effect in rubber sheets..... 403
Capacity of rubber mixtures to be moulded.. 466
Carbon blacks in GR-S..... 100
Chemical nature of the rubber-to-brass bond. 968
Coagulation of latex..... 491
Cold-compression sets of natural and synthetic vulcanizates..... 151
Comparison of different types of rubber obtained from the same field latex..... 848
Compression-adhesion test..... 223
sets, cold-, of natural and synthetic vulcanizates..... 151
Concentration of latex by means of electric currents of high frequency..... 486
Condensation reactions..... 329
Conductive rubber, electrically..... 667
Conference on postwar preparation of rubber. 865
Control of elongation in highly stretched cotton tire cord..... 253
Cooling facilities of rubber equipment..... 218
Copolymers, spectrophotometric determination of..... 1077

Page

Cord, adhesion of vulcanized rubber to..... 223
Course of autoöxidation reactions in polyisoprenes and allied compounds. XI. Double-bond movement during the autoöxidation of a monoölefin..... 1022
Cracking mechanism of rubber..... 406
Cryptostegia, extraction of rubber from..... 193
Crystalline components in stretched vulcanized rubber..... 1124
rubber, melting of..... 546
Crystallization of unvulcanized rubber at different temperatures..... 1145
Crystallizing rubberlike polymers, strength of 42

Dandelion, natural rubber from Russian.... 856
Deformation of rubberlike elastic bodies..... 525
Density of hard rubber..... 760
Deterioration, proöxygenic effect and resulting..... 296
surface, in sunlight of hard rubber..... 753
Dialkyl sulfide halides, formation of..... 287
Dienes, 1,5-carbalkoxy-substituted..... 14
polymerization of..... 1029
1,5-, ultraviolet absorption spectra of..... 23
Dilution of natural rubber..... 1
Dinitroso and related compounds..... 900
Differentiation of rubber and gutta hydrocarbons in plant materials..... 501
Dioximes and related compounds..... 900
Disulfide, tetramethylthiuram..... 1061
Dithiocyanogen, reactivity of isoprenic hydrocarbons towards..... 34
Double-bond movement during autoöxidation of a monoölefin..... 1022
refraction, dynamic, in rubber solutions... 360
Dynamic properties of rubbers..... 163

Ebonite, vulcanization of..... 948
Effect of moisture on GR-S. Rate of cure and physical properties..... 773
of pressure on the melting of crystalline rubber..... 546
Effects of molecular structure on physical properties of Butyl rubber..... 552
of proöxygenic substances on reclaimed rubber..... 123
of temperature and humidity on the physical properties of tire cords..... 233
Elastic bodies, deformation of..... 525
deformation and molecular weight in polyisobutylene..... 1047
Elasticity of a network of long-chain molecules. III..... 1009
theory of rubberlike..... 511
Electrically conductive rubber..... 667
Electrostatic and tensile properties of rubber and GR-S at elevated temperatures..... 428
Elongation, control of, in tire-cord..... 253
Entropies of dilution of natural rubber..... 1
Equipment, rubber, cooling facilities of..... 218
Estimation, direct, of absorption of oxygen by rubber..... 170
Evaluation of physical properties of rubber vulcanizates at low temperatures..... 915
Extraction of rubber from Cryptostegia grandiflora..... 193

Factors affecting results obtained with the Mooney viscometer..... 808
Fat acids of Hevea latex..... 788
Filler content of vulcanized rubber..... 482
Film thicknesses of polymeric substances.... 551
Films from GR-S latices..... 190
Foreign molecules dissolved in rubber..... 987
Free and forced vibration methods in the measurement of the dynamic properties of rubbers..... 163

Gas permeability and the microstructure of polymers..... 385
Gelation of rubber sols by ultraviolet light.. 632
Geranylamine, crystal structure of..... 351
GR-S, behavior under repeated stress cycles of carbon blacks in..... 417
effect of moisture on..... 773
latices, films from..... 190
tackiness of..... 1163
vulcanizates..... 696
Gutta hydrocarbons..... 501

Hard rubber, properties of.....753, 760
Hardening of crude rubber..... 400
Hardness tests at low temperatures..... 933
Heats of dilution of natural rubber..... 1
Hertzian spectrum of rubber and its micellar constitution..... 1085
Humidity, effect of, on tire cords..... 233

Improved brittle-point apparatus..... 844
Influence of milling on the plasticization of rubber..... 938
of vulcanization on the oxidizability of rubber. II. Vulcanizing agents other than sulfur..... 876
Infrared methods in structural examination of synthetic rubber..... 1113
spectra of compounds of high molecular weight..... 46
studies of vulcanization of rubber..... 66
Interaction between rubber and liquids. VII. Heats and entropies of dilution of natural rubber by various liquids..... 1
Isoprenic hydrocarbons, reactivity of..... 34

Ketene, behavior of..... 63

Latex, coagulation of..... 491
comparison of different types of rubber from same field..... 848
concentration of..... 486
Hevea..... 781
Hevea, polydispersion of..... 176
organic analysis of Hevea..... 788
particles, morphology of..... 187
quality of, and its chemical composition... 494
Latices, GR-S, films from..... 190
Length of long-chain molecules..... 1002
Long-chain molecules, elasticity of. III.... 1009
statistical length of..... 1002
Low temperatures, hardness tests at..... 933
of rubber vulcanizates..... 915

Magnetic anisotropy of rubber..... 349
Measurement of plasticity of Buna-S with the Williams apparatus..... 478
Mechanism of reënforcement. II..... 616
of rubber cracking..... 406
Melting of crystalline rubber, effect of pressure on..... 546
Metal, rubber-, bond..... 956
Methods of calculating and representing rheological properties, using data from the parallel-plate plastometer..... 461
Micellar constitution of rubber..... 1085
Microstructure of polymers..... 385
Milling, influence of, on the plasticization of rubber..... 938
Mobility of foreign molecules dissolved in rubber..... 987
Modified method for the direct estimation of the absorption of oxygen by rubber..... 170
Moisture, effect on GR-S of..... 773
Molecular fractions of rubber..... 602
processes during the deformation of rubberlike elastic bodies..... 525
structure, effects of, on physical properties of Butyl rubber..... 552
structure, in relation to surface film thickness of polymeric substances..... 551
weight in polyisobutylene..... 1047
weight of high polymers..... 599
Monoölefin, double-bond movement during autoöxidation of a..... 1022
Mooney viscometer..... 811
using the..... 821
Morphology of rubber latex particles..... 187
Moulded capacity of rubber mixtures..... 466

Natural rubber from Russian dandelion.....R 856

Page

Nature of dynamic double refraction in rubber solutions, and the shape of rubber molecules ... 360
New approach to the theory of rubberlike elasticity ... 511
New material: anhydride rubber. I ... 313
New method for determining the filler content of vulcanized rubber ... 482
Nonsulfur vulcanization. II. An experimental study ... 652

Olefinic peroxides, behavior of ketene towards ... 63
Olefins, behavior of ketene towards ... 63
Organic analysis of Hevea latex. VII. Fat acids, resin acids, sterols, and wax-alcohols. A preliminary note ... 788
VIII. Development of a general scheme of analysis ... 781
Oxidation of GR-S vulcanizates ... 696
Oxidative breakdown of rubber ... 267
Oxidizability, influence of vulcanization on ... 876
Oxygen, absorption of, by rubber ... 170

Packing of rubber ... 865
Permanent set at elevated temperatures ... 1099
Permeability, gas ... 385
Peroxides, olefinic, behavior of ketene towards ... 63
Photochemical breakdown of rubber ... 283
Photogelation of rubber sols in the absence of accelerators ... 645
Photogelling agents, rubber ... 394
Physical properties of films from GR-S latices ... 190
properties of rubber vulcanizates ... 915
Physical examination of brass deposits ... 208
Plant materials ... 501
Plasticity of Buna-S ... 478
Plasticization of rubber ... 938
Plastometer with uniform rate of shear ... 822
parallel-plate ... 461
Polychloroprene, x-ray study of ... 1088
Polydispersion of Hevea latex ... 176
Polyisobutylene, elastic deformation and molecular weight in ... 1047
Polyisoprenes, and allied compounds ... 287
autoöxidation reactions in ... 1022
double bond interaction of ... 14
structure of ... 14, 23, 351
Polymerization of dienes and vinyl compounds ... 1029
reactions ... 36
Polysulfide rubbers ... 1178
Preparation and packing of rubber ... 865
and properties of rubberlike high polymers. I. Polymerization of dienes and vinyl compounds in bulk ... 1029
Pressure, effect of, on melting of crystalline rubber ... 546
Principles of a method of vulcanization based on condensation reactions. Prosthesis and synesis ... 329
Procedure for determining physical properties of films from GR-S latices ... 190
Proöxygenic effect and the resulting deterioration of rubber ... 296
substances, effects of, on reclaimed rubber ... 123
Properties of hard rubber. XIV. Influence of some ingredients on surface deterioration in sunlight ... 753
XV. Influence of rubber-sulfur ratio and vulcanization time on the properties of pure rubber-sulfur compositions. (1) Chemical composition, density, and thermal expansion ... 760
Proportion of crystalline and amorphous components in stretched vulcanized rubber ... 1124
Prosthesis and synesis ... 329

Qualitative spot tests for rubber polymers ... 832

Radiomicrography. Study of rubber-sulfur mixtures by ... 392
Reactivity of isoprenic and analogous hydrocarbons towards thiocyanic acid and dithiocyanogen ... 34

Page

Recent advances in rubber analysis ... 792
Reclaimed rubber, effects of proöxygenic substances on ... 123
Reënforcement, mechanism of ... 616
Refraction, double, in rubber solutions ... 360
Relations between the quality of latex and its chemical composition ... 494
Report of Conference on postwar preparation and packing of rubber ... 865
Resin acids of Hevea latex ... 788
Resins, synthetic, vulcanization of rubber with ... 86
Rheological properties ... 461
Rubber photogelling agents. II ... 394
plastometer with uniform rate of shear—Shearing-cone plastometer ... 822
polyisoprenes and allied compounds. VIII. Formation of dialkyl sulfide dihalides, and its bearing on the problem of determining the unsaturation of vulcanized rubber ... 287

Shape of rubber molecules ... 360
Shearing-cone plastometer ... 822
Shellac as an ingredient of rubber compositions ... 125
Significance of the equation of state for rubber ... 1137
Single-cord compression adhesion test for evaluating the adhesion of vulcanized rubber to cord ... 223
Size-distribution curves in study of polymerization reactions ... 36
Sols, gelation of rubber, by ultraviolet light ... 632
photogelation of rubber ... 645
Solutions, double refraction in ... 360
Some infrared studies on the vulcanization of rubber ... 66
Specific heats of Hevea, GR-S and GR-I stocks ... 622
Spectra, infrared, of high molecular weight compounds ... 46
ultraviolet absorption of 1,5-dienes ... 23
Spectrography, ultraviolet ... 1051, 1061
Spectrophotometric determination of styrene content of butadiene-styrene copolymers ... 1077
Spectrum, Hertzian, of rubber ... 1085
Spot tests for rubber polymers ... 832
State of polydispersion of Hevea latex ... 176
Statistical length of long-chain molecules ... 1002
Sterols of Hevea latex ... 788
Strength of amorphous and of crystallizing rubberlike polymers ... 42
Stress cycles repeated, behavior of natural rubber and GR-S ... 417
-time-temperature relations in polysulfide rubbers ... 1178
Stretched vulcanized rubber, crystalline and amorphous components in ... 1124
Structural changes in vulcanization of Buna-S ... 534
examination of synthetic rubber by infrared methods ... 1113
Structure of polyisoprenes. I. Crystal structure of geranylamine hydrochloride ... 351
IV. Double bond interaction in certain carbalkoxy-substituted 1,5-dienes ... 14
V. Ultraviolet absorption spectra of certain carbalkoxy-substituted 1,5-dienes, and the charge-resonance spectra of glutaconic ester enolate ions ... 23
of synthetic rubbers. Ethylene polysulfide ... 1090
Study of rubber-sulfur mixtures by radiomicrography ... 392
of the mechanism of polymerization reactions by means of size-distribution curves ... 36
of the rubber-metal bond ... 956
of the various molecular fractions of rubber and their behavior during vulcanization ... 602
Styrene content of butadiene-styrene copolymers ... 1077
Sunlight, deterioration of hard rubber in ... 753
Surface film thicknesses of polymeric substances in relation to molecular structure ... 551
Synesis, prosthesis and ... 329

	Page
Tackiness of GR-S and other elastomers	1163
Temperature, effect of, on tire cords	233
Tensile properties of rubber	428
strength in relation to molecular weight of high polymers	599
Terminology of intrinsic viscosity and related functions	1092
Tests, spot, for rubber polymers	832
Tetramethylthiuram disulfide, transformation of	1061
Theory of permanent set at elevated temperatures in natural and synthetic rubber vulcanizates	1099
of rubberlike elasticity	511
Thermal breakdown of rubber	277
expansion of hard rubber	760
Thiocyanic acid and dithiocyanogen	34
Tire-cord, control of elongation in	253
cords, effects of temperature and humidity on	233
Types of rubber, comparison of different	848
Ultraviolet absorption spectra of 1,5-dienes	23
light, gelation of rubber sols in	632
spectrography	1051, 1061
Unsaturation of vulcanized rubber	287
Use and misuse of accelerated aging tests	447
Using the Mooney viscometer	821
Vibration methods, free and forced	163
Vinyl compounds	1029
Viscometer, Mooney, factors affecting results with	808
using the Mooney	821
Viscosity, intrinsic, and related functions	1092
Vulcanization, accelerated, of ebonite	948
nonsulfur	652
of anhydride rubber	319
of Buna-S, structural changes in	534
of molecular fractions of rubber	602
of rubber, infrared studies of	66
of rubber with synthetic resins	86
reactions in Butyl rubber. Action of dinitroso, dioxime, and related compounds	900
Vulcanizing agents, other than sulfur	876
Wax alcohols from Hevea latex	788
Weathering of soft vulcanized rubber	712
x-Ray investigation of the calender effect in rubber sheets	403
studies of synthetic rubbers. Polychloroprene	1088

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

Chairman.....W. A. GIBBONS, United States Rubber Co., New York
Vice-Chairman.....W. W. VOGT, Goodyear Tire & Rubber Co., Akron, Ohio
Secretary.....H. I. CRAMER, Sharples Chemicals, Inc., Philadelphia, Pa.
Treasurer.....C. W. CHRISTENSEN, Monsanto Chemical Co., Akron, Ohio
Sergeant-at-Arms.....M. F. TORRENCE
Directors.....HAROLD GRAY, A. H. NELLEN, FRED AMON, B. S. GARVEY, C. R. HAYNES, C. C. DAVIS, S. G. BYAM
Editor of *Rubber Chemistry and Technology*.....C. C. DAVIS
Advertising Manager of *Rubber Chemistry and Technology*.....S. G. BYAM

NEW BOOKS AND OTHER PUBLICATIONS

HIGH POLYMERS. Edited by Sumner B. Twiss. Published by Reinhold Publishing Corp., 330 West 42nd St., New York, N. Y. 6 x 9 in. 196 pp. $4.00.—The first phase in the development of a high polymer program at Detroit's Wayne University was the presentation of a Symposium on High Polymers in the spring of 1944. The symposium included a number of lectures, and because of the wide scope of these lectures and the universal interest which they aroused, it was felt that they should be presented to a wider audience through publication. This volume, the first in a series issued under the heading of "Advancing Fronts in Chemistry", contains the lectures in their entirety. Ten lectures are presented in the book: (1) *Molecular Structure and Mechanical Behavior of High Polymers*, by Herman F. Mark; (2) *The Relation Between Structure and Physical Properties of High Polymers*, by Samuel S. Kistler; (3) *Some Applications of Catalysis to Hydrocarbon Reactions of Importance in the Synthesis of High Polymers*, by Edgar C. Pitzer; (4) *Some Aspects of the Mechanism of Addition Polymerization*, by Charles C. Price; (5) *Polymerization as a Study of Reactions of Free Radicals*, by Frank R. Mayo; (6) *Molecular Size Distribution in High Polymers*, by Walter H. Stockmayer; (7) *Effect of Chain Length on Physical Properties of Cellulose Derivatives*, by Emil Ott; (8) *Nature of the Solid State of Chain Polymers*, by William O. Baker; (9) *Mechanical Properties of Concentrated Solutions of High Polymers*, by John D. Ferry; (10) *Some Concepts of Textile Fibers*, by Milton Harris. The book is adequately indexed for convenience. As an added feature, each chapter includes a photograph and brief biographical sketch of the contributor. [From *The Rubber Age* of New York.]

RUBBER IN ENGINEERING. Published by the British Ministry of Supply, Berkeley Court, Glentworth St., London, N.W., 1, England. 6¼ x 9½ in. 268 pp. plus Indexes.—Based on research carried out by Imperial Chemical Industries, Ltd., on behalf of the Controller of Chemical Research of the British Ministry of Supply and the directors of scientific research of the British

Ministry of Aircraft Production and the Admiralty, this book has been issued as one of the "Services Rubber Investigations" conducted throughout the wartime period in England. Designed to interest a wide variety of readers, its major purpose is to furnish engineers with a general survey of information available on the fundamental properties of rubber, and a considerable portion of the text is devoted to the theoretical aspects of the subject. It is divided into four sections: (1) The Rubberlike State; (2) General Properties of Rubber; (3) Rubber Technology; (4) Principles of the Design of Rubber Engineering Components. Appendices furnish data on dependence of deformation and mechanical losses upon time and temperature, the principal physical properties of rubber and their coefficients of change, the Dunlop Tripsometer, and the compression stress-strain relation. Author and subject indexes are included. [From *The Rubber Age* of New York.]

SCIENCE IN PROGRESS. Fourth Series. Edited by Geo. A. Baitsell. Published by Yale University Press, New Haven, Conn. Cloth, 6¼ x 9¾ inches, 346 pages. Illustrated. Price $4.00—This fourth volume of the "Science in Progress" series is an interesting and stimulating progress report, dealing in great detail with the advances made in the fields of chemistry, physics, mathematics, and physiology during the last year. Owing to the war, scientific research has received quite an impetus, and it is well apparent in this review that scientific research has been stepped up considerably. The men who have contributed to this volume are outstanding and world-known authorities in their particular fields, and many of them are Nobel prize winners. This book should be of interest to any chemist and scientist who wants to keep abreast of the latest developments in scientific research. The book will also be of interest to the layreader, however, as many of the scientific developments, discussed in these pages in detail, have received the attention of the daily press, where they were discussed in a less specific manner. Two papers, one on the psychological aspects of military aviation and another one on blood and blood derivatives, are very closely linked to the war, which has been the direct cause of these investigations. Of particular interest to scientific and technical workers in the rubber and plastics fields should be five of the eleven papers. One paper deals with the mathematical nature of physical theories. An elucidating chapter covers the relation between a function developed in theoretical physics and its mathematical expression. Along similar lines is an article by the Nobel prize winner, Peter Debye, on the magnetic approach to the absolute zero of temperature. Interesting new aspects of physical chemistry are discussed by H. Eyring, of Princeton, in a contribution about the drift toward equilibrium. Of a more general nature is an illustrated paper on high vacuum chemistry by K. C. D. Hickman, of Eastman Kodak Co. [From the *India Rubber World*.]

A.S.T.M. STANDARDS ON PLASTICS. American Society for Testing Materials, 260 S. Broad St., Philadelphia 2, Pa. May, 1945. Paper, 6 x 9 inches, 50 pages. Price $2.75 to nonmembers.—With the active cooperation of several of the standing committees of the A.S.T.M., Committee D-20 on Plastics has published in the latest approved form 109 test-methods, specifications, recommended practices, and definitions covering a wide range of plastics and related materials, with due consideration to even the most recent developments in the plastics field. Thirty-three test-methods were developed by Committee D-20, and there are 23 specifications giving quality requirements for different kinds and families of plastics (phenolics, alkyds, methacrylates,

melamines, cellulose, vinyl chlorides, etc.). Committee D-9 on Electrical Insulating Materials contributed 24 additional standards, and the other 24 standards were contributed by various other committees. Some of the subjects covered under test-methods include brittleness, color fastness, compressive strength, deformation, light diffusion, inflammability, flexural strength, specific gravity, tear resistance, water absorption, and numerous others. [From the *India Rubber World*.]

THE PLASTICS INDUSTRY. Plastics Materials Manufacturers' Association, 14th & K Sts., N.W., Washington 5, D. C. 5 x 7¼ in. 20 pp.—The purpose of this booklet is two-fold: to provide information which will be helpful in guiding those interested in the plastics business, and to correct certain widely-held misconceptions about the possibilities of the industry. Subjects taken up include the following: what plastics are, what the plastics industry is, major divisions of the industry, adhesive producers, specialty resins, replacement of metals by plastics, employment in the plastics industry, training for the plastics industry, increase in plastics materials during the war years, the role of the machinery manufacturer, and the postwar plastics industry. In connection with the subject of employment, there is a convenient listing of a few typical occupations in several main divisions of the industry, giving the title of the job and a brief description of the duties and approximate training required. [From *The Rubber Age* of New York.]

CHEMICAL ENGINEERING CATALOG: 1945–46. Published by the Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. 8½ x 11 in. 1708 pp.—This is the thirtieth annual edition of "The Process Industries' Catalog", and again it furnishes complete, revised, up-to-date information on equipment, supplies and raw materials for the chemical process industries. Following the style of the last several issues, it is divided into four major sections, *i.e.*, Trade Name Index, Equipment and Supplies, Chemicals and Materials, and Technical and Scientific Books. Classified indexes to the sections on equipment and chemicals are included in the respective sections, with manufacturers' catalogs representing the bulk of each section. [From *The Rubber Age* of New York.]

THE DIVISION OF RUBBER CHEMISTY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

Chairman.....W. A. Gibbons, United States Rubber Co., New York
Vice-Chairman.....W. W. Vogt, Goodyear Tire & Rubber Co., Akron, Ohio
Secretary.....H. I. Cramer, Sharples Chemicals, Inc., Philadelphia, Pa.
Treasurer.....C. W. Christensen, Monsanto Chemical Co., Akron, Ohio
Sergeant-at-Arms.....M. F. Torrence
Directors.....Harold Gray, A. H. Nelles, Fred Amon, B. S. Garvey, C. R. Haynes, C. C. Davis, S. G. Byam
Editor of *Rubber Chemistry and Technology*.....C. C. Davis
Advertising Manager of *Rubber Chemistry and Technology*.....S. G. Byam

NEW BOOKS AND OTHER PUBLICATIONS

Synthetic, A Great New Factor in Our Economic Life. By P. W. Litchfield. Published by the Goodyear Tire & Rubber Co., Akron, Ohio. 4 pages.—The future of America's synthetic-rubber industry is discussed briefly by the Chairman of the Board of the Goodyear Tire & Rubber Company. [From *The Rubber Age* of New York.]

World Rubber and Its Regulation. By K. E. Knorr. Published by Stanford University Press, Stanford University, California. 6 x 9 in. 265 pp. $3.00.—This book is a product of a research program on international commodity agreements conducted by the Food Research Institute of Stanford University. The Institute was forced to look beyond food products for pertinent examples of commodity control, and rubber naturally fell beneath its microscope. The book traces the growth of the natural rubber industry, its welfare between two wars, and the rise of the synthetic rubber industry. Particular emphasis is, of course, placed on the International Rubber Regulation Agreement and other attempts to "control" the market. The author presents a significant survey of rubber economy in the years to come, the competition of natural and synthetic rubber, their sources and markets, and the possibilities of development of new uses and other alternatives for consuming the rubber output. How the United States may be protected against future attempts at international control, how large a rubber stockpile should be accumulated, how far, if at all, synthetic rubber plants should be or need be subsidized to keep functioning, are among the subjects discussed. Since a national rubber policy for the United States is currently pending, this book is most timely. [From *The Rubber Age* of New York.]

Science and Scientists in the Netherlands Indies. Edited by Pieter Honig and Frans Verdoorn. Published by The Board for the Netherlands Indies, Surinam and Curaçao, and G. E. Stechert & Co., New York, 1945.

Cloth, 7 x 10¼ in. XXIV + 491 pp. Illustrated. Price $4.00.—The editors state that they have endeavored to picture the development and status of some of the natural sciences, both pure and applied, in the Netherlands Indies. To this end they have included: (1) original articles on the development or status of various sciences; (2) reprints of accounts published elsewhere in Dutch but now in English; (3) accounts of travels by visitors, with glimpses, some scientific of life and nature; (4) short articles of concern in promoting closer relations of North America and the Netherlands Indies, and (5) scientific institutions, societies, and workers at the time of the Japanese invasion. There are about seventy authors, and the book is illustrated with numerous full-page plates, many of historical and artistic value. Of particular interest to rubber chemists and technologists and to other members of the rubber industry are articles on "Work of the West Java Research Institute in Buitenzorg", "History of Rubber Cultivation and Research in the Netherlands Indies," "Scientific Institutions, Societies and Research Workers in the Netherlands Indies", and "The Central Depository Library for the Netherlands Indies in New York City". [C. C. Davis.]

ADVANCING FRONTS IN CHEMISTRY. Volume I. HIGH POLYMERS. Sumner B. Twiss, Editor, Department of Chemistry, Wayne University, Detroit, Michigan. Reinhold Publishing Corporation, 330 West 42d Street, New York, New York, 1945. 196 pp. 15.5 x 23.5 cm. Price, $4.00.—This book contains ten lectures at Wayne University in 1944, with the objective of presenting unified concepts of certain phases of polymer science. Because of the limitations of space, the first two chapters by Mark and Kistler, dealing with the general relationships between polymer structure and physical properties, are neither descriptive enough to be of much help to the beginner nor mathematical enough to satisfy the expert. Contrasted with these, the mathematical but very lucidly presented short chapter by Stockmayer makes an excellent basis for classroom presentation of condensation polymerization, and at the same time should be read by any polymer chemist who has not followed Flory's and Stockmayer's original papers.

The longer chapters dealing with physical properties of polymers are more successful than the first two. In particular, Baker gives a great many data on the structure and properties of polyamides and some other polymers, showing how the manner of packing of the chains and the physical properties vary in an understandable manner with apparently minor changes of structure. Ott has kept in mind the requirements of the beginner as well as the advanced worker in his discussion of the reasons why the physical properties of polymers vary with chain length and chain-length distribution. He also gives enough data on strength, flexing resistance, elongation and flow properties of cellulose derivatives to make his story complete. A somewhat shorter chapter, by Harris, on fibers deals mainly with the very interesting effects of disulfide cross links on wool properties. The chapter on variation of mechanical properties of concentrated solutions with rate of application of load, illustrated by Ferry with a few graphs, is tantalizing. The treatment is good, though elementary. However, the author has missed many opportunities for pointing out to the worker in the field how to apply to everyday problems the concepts illustrated by him.

Two purely chemical chapters, by Price and by Mayo, both dealing with free radical polymerization, deserve special note. Price shows how peroxides

form free radicals, and how these free radicals are consumed by chain initiation, recombination, disproportionation and transfer reactions. He further discusses the connection between inhibition and the stabilization of free radicals by resonance. Mayo has used the concepts of varying reactivity and relative stability of free radicals to show that chain transfer may be treated quantitatively, and that copolymerization cannot be studied effectively until we are able to measure free radical concentration.

The remaining chapter, by Pitzer, on catalysis of hydrocarbon reactions to produce monomers, will not be of interest to the average polymer chemist.

The reviewer would like to repeat the frequent request that chapter headings be repeated at the top of the page, particularly if references are given at the end of the chapter, as in this case. He also feels that editors of such collections should make sure that the contributions are more consistent in type of treatment than is the case with this book.

At the suggestion of the author, the following corrections should be noted: Page 84, line 20, should read "The weight-average is normally no greater than twice the number-average". Page 97, line 24, "weight-average" should be "number-average". Page 101, line 1, should be "— the logarithm of the viscosity of the plastic melt increases linearly with the square root of the chain length".

This book should be available to every teacher and worker dealing in fundamental polymer science. The price is too high and the treatment often too brief to justify use as a text or reference book. [H. M. Spurlin in the *Journal of the American Chemical Society*.]

PLASTICS IN PRACTICE. A Handbook of Product Applications. John Sasso and Michael A. Brown, Jr. McGraw-Hill Book Co., Inc., New York, N. Y. 1945. Cloth, 7½ x 10½ inches. 192 pages. Price $4.00—The authors of this book have done a commendable job in assembling information for the reader who is not an expert in plastics, but who, as an engineer, designer, or businessman, is interested in plastic materials primarily from the viewpoint of what use they may be to him in improving his product, increasing sales, and lowering costs. To answer these questions in the quickest and most practical manner, the properties of the various plastics and fabricating methods are discussed in direct relation to proved, successful commercial uses. More than 100 case studies have been assembled, each typifying the use of a particular plastic or fabricating method.

A brief introductory section sets up a frame of reference by including with the short explanation of the various groups of thermosetting and thermoplastic materials and their processing methods, specific case numbers, which in the next section of the book show how, for example, cotton-flock-filled phenolic plastic compound is used for the compression-molded vacuum-cleaner motor hood or how vinyl chloride polymers and copolymers are used for wire and cable insulation. These case histories are followed by a section of new developments which describes both new materials and new methods. Included here are discussions of nylon and new styrene polymers and copolymers for molding, and a new styrene elastomer, the use of low-viscosity vinyl butyrals combined with GR-S for shoe soles, silicone resins, post-formed laminates, pulp-preform molded parts, and resin-paper sheets.

Realizing the necessity of defining what was meant by the word "plastics" in planning the coverage of this book, the authors arrived at the following

definition as far as their book was concerned: "Synthetic organic polymers processed into parts or articles by molding, laminating, casting, machining, not including surface finishes, fibers or those compounds commonly known as synthetic rubber." [From the *India Rubber World.*]

JAR RINGS FOR USE IN HOME CANNING. Their Testing and a Proposed Specification. Rolla H. Taylor, Helen G. Wheeler, and Frances Benedict, National Bureau of Standards, Washington, D. C. Miscellaneous Publication M181. 6 x 9 in. 20 pp. (Available from Superintendent of Documents, Washington 25, D. C., at 10c per copy.)—This pamphlet presents the results of an investigation of jar rings which was undertaken by the U. S. Department of Agriculture in collaboration with manufacturers and the National Bureau of Standards. Rings were analyzed for rubber content, and measurements were made of their tensile strength, ultimate elongation, stress at 100% elongation, swelling on processing, indentation by a ring simulating a jar cap, and hardness. The results of the investigation are expressed in terms of a proposed specification for jar rings. Topics covered include: variations in jars and tops, laboratory processing, methods of measuring physical properties, chemical analysis, taste imparted to canned food by jar rings, aging, canning tests as a basis for development of a jar-ring specification, and correlation of properties and composition with results of canning tests. [From *The Rubber Age* of New York.]

PATENTS AND YOUR TOMORROW. National Association of Manufacturers, 14 West 49th St., New York 20, N. Y. 6 x 8½ in. 24 pp.—The importance of patents to science and invention and to technological progress in general is emphasized in this booklet, which also includes a comprehensive quiz on patents answering questions on the various aspects and accomplishments of the patent system. Definitions are given of such terms as cross-licensing, restrictive licensing, cartels, compulsory licensing, and exchange of patents, with industry's position indicated on each subject. [From *The Rubber Age* of New York.]

MAJOR INSTRUMENTS OF SCIENCE AND THEIR APPLICATIONS TO CHEMISTRY. Edited by R. E. Burk and Oliver Grummitt. Published by Intersicence Publishers, Inc., 215 Fourth Ave., New York 3, N. Y. 6 x 9 in. 151 pp. $3.50—This is Volume 4 of the series of "Frontiers in Chemistry" being published under the auspices of Western Reserve University. This series is composed of lectures presented by leading experts in various fields, and their publication makes them available to a much wider audience. The current volume contains six lectures: Electron Diffraction and the Examination of Surfaces, by Lester H. Germer; The Electron Microscope and Its Applications, by L. Marton; X-Ray Diffraction and Its Applications, by Maurice L. Huggins; Chemical Spectroscopy, by Wallace R. Brode; Application of Absorption Spectra to Chemical Problems, by Wallace R. Brode; The Infrared Spectrometer and Its Applications, by R. Bowling Barnes. Brief biographies of each lecturer are given. A subject index is included. [From *The Rubber Age* of New York.]

SURFACE-ACTIVE AGENTS, THEORETICAL ASPECTS AND APPLICATIONS. By C. B. F. Young, Ph.D. and K. W. Coons, Ph.D. Chemical Publishing Co., Inc., Brooklyn, N. Y., 1945. 362 pp. Price, $6.00.—This book was written,

as stated in its preface, to present information as to origin, effects and utilization of surface tension phenomena in a diversity of industrial fields. Part I is devoted to a discussion of the theory of surface tension, its determination, and the structure of wetting agents and specific surface tension agents. Part II covers such topics as emulsions, metal cleaning, cosmetics, leather, flotation, inks, textiles, cutting oils, adhesives, foods, lubrication and soldering.

The first chapter is devoted to a review of the theoretical considerations pertaining to surface tension as can be found in any good textbook on colloid chemistry. In the discussion of the determination of surface tension, the authors have seemingly misinterpreted the work of Harkins and Brown, who developed the drop weight and not the drop number method. The authors classify rubber latex as a protective colloid (p. 162). The authors seemingly have overlooked the fact that rubber latex itself is a protected dispersion. The chapter on cosmetics (p. 186 *ff.*) uses a terminology which certainly is beyond the scope of this book and will, therefore, stun many a reader. The chapter on flotation (p. 214 *ff.*) also contains several misleading statements. In the case of galena, the air does not displace the water, but the hydrophobic property of its surface prevents wetting.

Rubber latex (p. 321) can certainly not be classified as adhesive in the sense in which this term is normally used.

These are just a few examples picked at random, but what is most deplorable is the title, because it is misleading. Only Chapter III actually deals with the structure of agents which reduce the surface tension of a system, and only such compounds can be classified as surface active agents.

This rather high-priced book may be of value to someone who wants to get a quick survey of the fields discussed, but anyone who is interested in their fundamentals will not get what he has been looking for. [Ernst A. Hauser in the *Journal of the American Chemical Society.*]

PHYSICAL METHODS OF ORGANIC CHEMISTRY. Vol. I. Edited by Arnold Weissberger. Published by Interscience Publishers, Inc., New York. 6 x 9 in. 736 pp. $8.50.—This is the first of two volumes designed to bring together between covers the numerous physical methods which are often applied by chemists to problems involving organic chemistry. It is composed of contributions from experts in various fields, and includes descriptions of tested methods, the theoretical background for understanding and handling these methods, and the information necessary for a critical evaluation of the experimental results. This first volume consists of 16 chapters:

Determination of Melting and Freezing Temperatures, Evald L. Skau and Helmut Wakeham; *Determination of Boiling and Condensation Temperatures,* W. Swietoslawaski; *Determination of Density,* N. Bauer; *Determination of Solubility,* Robert D. Vold and Marjorie J. Vold; *Determination of Viscosity,* H. Mark; *Determination of Surface and Interfacial Tension,* William D. Harkins; *Determination of Properties of Monolayers and Duplex Films,* William D. Harkins; *Determination of Osmotic Pressure,* R. H. Wagner; *Determination of Diffusivity,* A. L. Geddes; *Calorimetry,* Julian M. Sturtevant; *Microscopy,* Edwin E. Jelley; *Determination of Crystal Form,* M. A. Peacock; *Crystallochemical Analysis,* J. D. H. Donnay; *X-Ray Diffraction,* I. Fankuchen; *Electron Diffraction,* L. O. Brockway; *Refractometry,* N. Bauer and K. Fajans. [From *The Rubber Age* of New York.]

STANDARDS ON ELECTRICAL INSULATING MATERIALS (WITH RELATED INFORMATION). Published by the American Society for Testing Materials, 260 So. Broad St., Philadelphia 2, Penna. 6 x 9 in. 560 pp. $3.25—This special compilation, prepared by the American Society for Testing Materials' Committee D-9 on Electrical Insulating Materials, gives in their latest form the more than seventy-five widely used specifications and test methods covering electrical insulating materials and related products. In addition to the standards developed by this committee, others pertain to certain plastics, rubber, textiles and paper products. Included also are several reports covering the significance of tests of insulating materials, a proposed method of testing askarels, and most recent recommendations affecting standards on electrical insulating materials. The reports discussing the tests cover dielectric strength, impact, tensile strength, power factor, resistivity, and for insulating liquids several others, such as pour point, viscosity, etc. There are groups of standards covering insulating varnishes, paints, lacquers and their products. Specifications and methods on insulating paper, mica products, rubber products, textile materials, etc., are grouped. [From *The Rubber Age* of New York.]

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

Chairman.....W. A. Gibbons, United States Rubber Co., New York
Vice-Chairman.....W. W. Vogt, Goodyear Tire & Rubber Co., Akron, Ohio
Secretary.....H. I. Cramer, Sharples Chemicals, Inc., Philadelphia, Pa.
Treasurer.....C. W. Christensen, Monsanto Chemical Co., Akron, Ohio
Sergeant-at-Arms.....M. F. Torrence
Directors.....Harold Gray, A. H. Nelles, Fred Amon, B. S. Garvey, C. R. Haynes, C. C. Davis, S. G. Byam
Editor of *Rubber Chemistry and Technology*.....C. C. Davis
Advertising Manager of *Rubber Chemistry and Technology*.....S. G. Byam

NEW BOOKS AND OTHER PUBLICATIONS

Specifications for Government Synthetic Rubbers. Effective January 1, 1946. Reconstruction Finance Corp., Office of Rubber Reserve, Washington, D. C. 46 pages.—These specifications were issued upon the request and with the approval of the Committee on Specifications for Synthetic Rubbers. Further studies are being made by the Committee, and revisions and additions will be issued from time to time. The booklet is divided into five sections. The first section, on specification limits, gives the requirements for GR-S, GR-S-10, GR-S-25, GR-S-38, GR-S-50,GR-S-65, GR-S-85, GR-S-AC, GR-S-12AC, GR-S-20AC, GR-S-Black-1, GR-S-Black-1AC, GR-M, GR-M-10, GR-I, and GR-A. The second section covers methods of sampling and sample preparation for the different types of rubbers. The third section, on chemical methods, includes procedures for determination of volatile matter, ash, E-T-A extract, fatty acid, soap, and carbon black. The fourth section, on physical test methods, treats of Mooney viscosity, plasticity-recovery, water absorption, viscosity and gelling of GR-S solution, and properties of the vulcanizate, including recipe and mixing procedure, equipment, and curing and testing procedures. The fifth section is an appendix listing suppliers of RRC standard compounding ingredients. [From the *India Rubber World*.]

Le Caoutchouc d'Hévéa: Initiation aux Méthodes d'Exploitation en Indochine. (Hevea Rubber: Introduction to Methods of Cultivation in Indo-China.) Institut Français du Caoutchouc, Paris, 1945; pp. 159 + 74 plates + 48 figs. + 3 maps. Price, 400 francs.

This well produced book, published by the Institut Français du Caoutchouc, is primarily for the young planter, young botanist or young agriculturist who on leaving college has acquired no specialized information on the subject. It is essentially "un ouvrage d'initiation", a book of initiation into the cultivation of rubber plantations which has been produced by the collaboration of the

planters and the Institute. The book will not only prove of interest to the future planters of Heveas, but to Colonials not engaged in rubber planting, but anxious to have information of neighboring activities, and also to residents in the home country who are engaged in the various branches of the rubber industry and wish to extend their knowledge of raw rubber production. The work is divided into three parts. In the first part, prepared by Jacques Le Conte, following a brief history of rubber, appears a description of the *Hevea brasiliensis* and other rubber yielding plants and the development of plantations. The functions, collection and composition of latex are described.

The second and by far the largest part by H. Reynauld deals with the exploitation and cultivation of rubber from the forests of the Amazon and Africa to the plantations. The climatic and soil conditions suitable for plantations are discussed, together with the selection and reproduction of high yielding trees, the density of planting, diseases of rubber trees, insect pests, harvesting the latex, coagulation, sheeting, crêpe rubber, smoked sheet, concentrated latex, powdered rubber.

It is suggested that Indo-China is suitable for larger plantations than the more mountainous Malaya.

The third part, compiled by Georges Colin, describes briefly the properties of raw and vulcanized rubber and the basic methods used in the manufacture of rubber articles. Rubber solutions, latex, ebonite and rubber derivatives are mentioned.

A list is given of the French technical literature consulted during the preparation of the book.

The book is well printed, profusely illustrated with plates and figures, and is a most useful account of the planting side of the industry, but it has one fault; there is no subject index, although it may be claimed that the detailed chapter contents, to a certain extent, overcome this difficulty. [From the *Transactions of the Institution of the Rubber Industry.*]

JOURNAL OF COLLOID SCIENCE, Victor K. LaMer, Editor-in-Chief, *et al.* Academic Press, Inc., Publishers, 125 East 23rd St., New York 10, N. Y. Volume I, No. 1, January, 1946. Published bimonthly at $10.00 a year.—This new publication, with Professor LaMer of Columbia University as Editor-in-chief, will contain original papers, letters to the Editor and book reviews. In addition to Professor LaMer, the editors are T. R. Bolam of Edinburgh, E. F. Burton of Toronto, R. M. Fuoss of New Haven, H. R. Kruyt of Utrecht, J. W. McBain of Palo Alto, E. K. Rideal of Cambridge, William Seifriz of Philadelphia, A. W. Thomas of New York, Arne Tiselius of Upsala and Harry B. Weiser of Houston, an impressive list. There is also a consulting committee composed of W. T. Astbury, J. J. Bikermann, W. Clayton, P. Debye, W. Feitknecht, Alexander Frumkin, William D. Harkins, Ernst A. Hauser, Wilfried Heller, J. N. Mukherjee, F. F. Nord and The Svedberg.

The papers in the first number are: "Contraction and the Chemical Structure of the Muscle Fibril" by A. Szent-Györgi; "Polarization and Permeability" by M. Spiegel-Adolf and E. A. Spegel; "Torsion in Protoplasm" by William Seifriz; "Adsorbed Nitrate Ions in Relation to Plant Growth" by H. Jenny; "Surface Films of Polymers" by D. J. Crisp; "Monodispersed Hydrophobic Colloidal Dispersions and Light-Scattering Properties. I." by Victor K. LaMer and Marion D. Barnes; "Monodispersed Hydrophobic Colloid Dispersions and Light-Scattering Properties. II." by Marion D. Barnes and Victor K. LaMer; "The Method of Purifying and Concentrating Colloidal Dispersions

by Electrodecantation" by Paul Stamberger; "Structure of Soap Micelles as Indicated by X-Rays and Interpreted by the Theory of Molecular Orientation. II." by William D. Harkins, Richard W. Mattoon and Myron L. Corrin. One wonders why there was not a paper on plastics in the first number and why there were two papers by the Editor-in-Chief. Plastics is a very important field in the colloid science of today. [Wilder D. Bancroft in the *Journal of the American Chemical Society.*]

COMPOUNDING MATERIALS USED IN THE RUBBER INDUSTRY (Classification and Health Hazards). Part 1—Accelerators, Antioxidants, and Retarders. Rubber Section, National Safety Council, Chicago, Ill. Industrial Safety Series No. Ru. 1—Part 1. 12 pages.—This booklet lists chemicals and trade names, with chemical compositions, of many accelerators, antioxidants, and retarders used in the rubber industry, together with a description and classification of the health hazards according to defined classifications. The information is based on data from questionnaires submitted to manufacturers and users of the compounds, and from available published material. A list of references to the literature is appended. [From the *India Rubber World.*]

PLASTICS AND THE PLASTICS INDUSTRY. George S. Armstrong & Co., Inc., 52 Wall St., New York 5, N. Y. 8½ × 11¼ in. 88 pp.—The seventh in a series of booklets published under the general heading of "An Engineering Interpretation of the Economic and Financial Aspects of American Industry", this booklet discusses the progress in the development of plastic materials and their conversion into usable form or applications. Divided into four sections, it covers the following: (1) Historical development and representative uses of plastic materials, including natural and chemical plastics; (2) The manner in which the fundamental natural resources are processed and the desired derivatives obtained from them for the manufacture of plastics; (3) Physical properties, production statistics, and postwar prospects of plastic materials; (4) The organization of the plastics industry, and the methods of converting plastic materials into usable end products. [From *The Rubber Age* of New York.]

Publications of the Midwest Rubber Reclaiming Co., East St. Louis, Ill. GR-I INNER TUBE COMPOUNDS CONTAINING BUTYL TUBE RECLAIM. Report No. 4. 4 pages.—Experimental formulations and test results are given to show that the use of limited amounts of Butex, a Butyl tube reclaim, in GR-I inner tube compounds seems to aid processing, imparts better aging characteristics, and does not adversely affect physical properties. BUTYL TUBE RECLAIM USED AS REPLACEMENT FOR GR-I. Report No. 5. 4 pages.—Test descriptions and results evaluate the effect of replacing GR-I with increasing amounts of Butex while the same total carbon black content is maintained in all compounds. Plasticity and scorchiness remain unaltered, but increasing the reclaim content progressively decreases the deterioration of physical properties after oven aging, and decreases tensile, elongation, hardness, and set values before aging. The modulus reaches a maximum at 50 per cent replacement; while the rebound values remain constant for all compounds. [From the *India Rubber World.*]

ORGANIC PREPARATIONS. By Conrad Weygand. Published by Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y. 6 × 9 in. 534 pp.

$6.00.—This is a translation of Part II, "Reaktionen", of the author's "Organisch-chemische Experimentierkunst", originally published in Leipzig in 1938, the translation being made and published with the consent of the Alien Property Custodian. Its treats with laboratory procedure in organic chemistry as an experimental art, and traces the course of laboratory work from the construction of apparatus through analysis and physical identification. The subjects include the formation of carbon-hydrogen, carbon-halogen, carbon-oxygen, and carbon-carbon bonds; cleavage of carbon-oxygen and carbon-nitrogen bonds; formation of organic derivatives of trivalent nitrogen and of carbon-tentavalent nitrogen linkages; carbondivalent and carbon-hexavalent sulfur bonds; fission of carbon-carbon bonds; and rearrangements of carbon compounds with the exception of steric rearrangements. A subject index is included. [From *The Rubber Age* of New York.]

THE ELECTRON MICROSCOPE. An Introduction to its Fundamental Principles and Applications. Second Edition. E. F. Burton and W. H. Kohl. Reinhold Publishing Corp., 33 W. 42nd St., New York, N. Y. February, 1946. Cloth, 6 by 9 inches. 328 pages. Price $4.—This second edition presents many rearrangements and revisions of the text of the previous edition to attain greater coherence in the presentation of the subject matter. The detailed description of the Johannson-Bruche electrostatic electron microscope and other material considered too specialized for the scope of the book have been eliminated. The chapter on the history of the electron microscope has been deleted and part of its contents incorporated into other chapters. The chapters on electron optics have been enlarged, and the material on electron lenses has been consolidated therein. The chapter on the compound magnetic electron microscope has been rewritten completely, and much new material added. The chapter on the applications of the electron microscope has also been largely rewritten.

After a review of light, vision, light microscopes, and light waves, succeeding chapters discuss the electron, electron emission, the dual theories of light and the electron, and the motion of electrons in electrical and magnetic fields. Following two chapters on electron optics, which cover magnetic and electrostatic focussing, there are individual chapters on the electrostatic electron microscope, the magnetic electron microscope, and the 1944 Toronto microscope. Concluding the book are highly interesting chapters on useful magnification, the use of the electron microscope, and its practical applications, including the study of carbon black, fillers, clays, and other products of interest to the rubber industry. The many plate illustrations include photographs of polyvinyl chloride, natural rubber, Buna-S and Thiokol latices, Micronex and P-33 carbon black particles, magnesia, bentonite, kaolin, asbestos fiber, and other minerals. The volume also contains an extensive bibliography and comprehensive indices.

The book is intended for the nontechnical reader, and the physical principles on which the operation of the electron microscope is based are presented with this aim in mind. The subject matter is such, however, that a large amount of ground must be covered and many intricate problems solved. The presentation and assimilation of the material are greatly facilitated by the use of extensive illustrations and drawings. The book should be of interest to members of various professions in which the electron microscope has made, or promises to make, considerable contributions in specialized research. [From the *India Rubber World*.]

CHEMICAL CONSTITUENTS [COMPONENTS] OF PETROLEUM. By A. N. Sachanen. Published by Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. 6 × 9 in. 450 pp. $8.50.—This book represents an exhaustive study of the basic chemistry of petroleum, including the most recent findings on this complex subject. A considerable part of the book is confined to individual hydrocarbons and compounds, which have been separated from petroleum, as well as to the methods of separation and identification. Data on the content of various types of hydrocarbons and other components, expressed in terms of ring analysis and of conventional classes, together with the methods for determining the structures and classes, make up a large part of the volume. There are ten chapters in all, with extensive literature references supplied at the end of each chapter. A short section on the derivation of synthetic rubber from petroleum-based butadiene is included in the chapter on "Hydrocarbons of Synthetic Distillates". [From *The Rubber Age* of New York.]

COLORIMETRY FOR CHEMISTS. By M. G. Mellon, Professor of Analytical Chemistry, Purdue University. The G. Frederick Smith Chemical Company, 867 McKinley Avenue, Columbus, Ohio, 1945. 15.5 × 23 cm. 133 pp. 51 figs. Price, $1.00 for bound copies. Paper copies free on request.—The still growing importance of optical methods for quantitative analysis is exemplified by this compact and suggestive volume. After a careful delineation of the scope of colorimetric methods, there is a description of typical instruments, their manipulation and limitations. Much attention is devoted to tabulation and plotting of experimental data, and the relative advantages of various coördinates are discussed. There is a section dealing with color analysis and psychophysical specification. The final chapter outlines a number of experiments designed for development of technical skill. The bibliography of two hundred and fifty references is well chosen and up to date. Those who digest this booklet can undertake colorimetric and spectrophotometric procedures with added efficiency and confidence. [George S. Forbes in the *Journal of the American Chemical Society*.]

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

Chairman . . . . . W. W. Vogt, Goodyear Tire & Rubber Co., Akron, Ohio
Vice-Chairman . . . . . H. E. Outcault, St. Joseph Lead Co., New York, N. Y.
Secretary . . . . . C. R. Haynes, Binney & Smith Co., New York, N. Y.
Treasurer . . . . . C. W. Christensen, Monsanto Chemical Co., Akron, Ohio
Sergeant-at-Arms . . . . . L. M. Baker
Directors . . . . . W. A. Gibbons, R. A. Schatzel, G. L. Allison, A. M. Neal, G. H. Swart, C. C. Davis, S. G. Byam
Editor of *Rubber Chemistry and Technology* . . . . . C. C. Davis
Advertising Manager of *Rubber Chemistry and Technology* . . . . . S. G. Byam

OFFICERS OF LOCAL RUBBER GROUPS

Akron

Chairman . . . . . Jack R. Moore, Sales Manager
Standard Chemical Co.
609 Akron Savings & Loan Building
Akron 8, Ohio

Vice-Chairman . . . . . Roy M. Vance
General Tire & Rubber Co.
Englewood Ave.
Akron 9, Ohio

Secretary . . . . . Henry F. Palmer, Chemical Engineer
519 Mineola Ave.
Akron 2, Ohio

Boston

Chairman . . . . . James R. Geenty, Chief Chemist
Goodall Sanford, Inc. (Reading Division)
Ash Street
Reading, Mass.

Vice-Chairman . . . . . Charles E. Reynolds, Research Director
Cambridge Rubber Co.
748 Main Street
Cambridge 39, Mass.

Secretary-Treasurer . . . Richard K. Patrick, President
Vulplex, Inc.
Bates St.
North Abington, Mass.

BUFFALO

Chairman . . . . . E. C. SIVERSON, Superintendent
Buffalo Weaving & Belting Co.
260 Chandler Street
Buffalo 7, N. Y.

Vice-Chairman . . . . . EDWARD SVERDRUP, Director of Research
U. S. Rubber Reclaiming Co.
Babcock and Hanna Sts.
Buffalo 5, N. Y.

Secretary-Treasurer . . . E. R. BRIGGS
Hewitt Rubber Corp.
240 Kensington Ave.
Buffalo 5, N. Y.

CHICAGO

Chairman . . . . . FRANCIS S. FROST, JR., Chief Chemist
Frost Rubber Works
1415 N. Dayton St.
Chicago 22, Illinois

Vice-Chairman . . . . . W. M. CRUMPLER, Branch Manager
Geo. F. Mepham Corp.
400 W. Madison Ave.
Chicago 6, Illinois

Secretary-Treasurer . . . ROBERT C. DALE, Chief Chemist
Inland Rubber Corp. Division
146 West 27th St.
Chicago, Illinois

CONNECTICUT

Chairman . . . . . WILLIAM J. O'BRIEN, JR., Chief Chemist
Seamless Rubber Co.
253 Hallock Ave.
New Haven 3, Conn.

Vice-Chairman . . . . . RAYMOND H. DUDLEY, Chief Chemist
Whitney Blake Co.
1565 Dixwell Ave.
Hamden, Conn.

Secretary . . . . . ALFRED J. JENNINGS
E. I. du Pont de Nemours & Co.
85 Mill Plain Road
Fairfield, Conn.

Treasurer . . . . . EDWARD J. BUTLER
General Electric Co.
1285 Boston Avenue
Bridgeport 2, Conn.

DETROIT (RUBBER AND PLASTICS)

Chairman . . . . . JOHN R. SHROYER
R. T. Vanderbilt & Co., Inc.
18727 Bretton Drive
Detroit, Michigan

1st Vice-Chairman....J. Paul Wilson
Ford Motor Company
Miller Road, Gate 4
Dearborn, Michigan

2nd Vice-Chairman...Gordon Saunders
Dodge Brothers
7900 Joseph Campau
Detroit, Michigan

Secretary-Treasurer...Edward J. Kvet, Tech. Supt.
Baldwin Rubber Co.
366 E. South Boulevard
Pontiac 12, Michigan

Los Angeles

Chairman.....C. M. Reinke
Reinke, Heller and Amende, Inc.
1925 E. Olympic Blvd.
Los Angeles 21, California

Vice-Chairman.....Phillip W. Drew, Chief Chemist
Goodyear Tire & Rubber Co.
6701 S. Central Ave.
Los Angeles 1, California

Assoc. Chairman.....Curtis R. Wolter
U. S. Rubber Co., Synthetics Division
P. O. Box 118
Torrance, California

Secretary.....H. Carroll Walker
Kirkhill Rubber Co.
811 West 58th St.
Los Angeles 37, California

New York

Chairman.....George J. Wyrough, Asst. Vice-President
Whitehead Bros. Rubber Co.
Whitehead Rd.
Trenton 4, N. J.

Vice-Chairman.....Simon Collier, Mgr. Product Control
Johns Manville Corp.
22 East 40th St.
New York 16, N. Y.

Secretary .....Peter P. Pinto, General Manager
The Rubber Age
250 West 57th Street
New York 19, N. Y.

North California

Chairman.....L. I. Shafer, General Manager
American Rubber Mfg. Co.
1145 Park Ave.
Oakland 8, California

Vice-Chairman.....GEORGE B. FARWELL
Reliance Rubber Co.
1515 Powell St.
Oakland 8, California

Secretary-Treasurer...B. O. BLACKBURN
Shell Development Corp.
Emeryville, California

PHILADELPHIA

Chairman.....W. B. MONROE, Chief Chemist
Linear, Inc.
6464 State Road
Philadelphia 35, Penna.

Vice-Chairman.....LAWRENCE K. YOUSE, Chief Chemist
L. H. Gilmer Co. Division
Cottman and Keystone Sts.
Tacony 35, N. Y.

Secretary.....T. T. MACCONNELL
U. S. Rubber Reclaiming Co.
500 Fifth Ave.
New York 18, N. Y.

Treasurer.....WILLIAM B. DUNLOP, JR.
Lee Rubber & Tire Co.
Hector St. Extension
Conshohocken, Penna.

RHODE ISLAND

Chairman.....SHERMAN I. STRICKHOUSER, Asst. Factory Manager
United States Rubber Co.
Eagle St.
Providence, R. I.

Secretary.....HAROLD W. GREENUP, President
Pilgrim Latex Thread Co.
1 Shore St.
Fall River, Mass.

SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

ATLANTIC CITY, N. J.

APRIL 10–12, 1946

The American Chemical Society met in Atlantic City, N. J., April 8–12, 1946, for its 109th Convention. The Division of Rubber Chemistry participated in this meeting with a four-day technical program. This meeting marked the resumption of activities by the Division after a two years' suspension due to the war. With the relaxation of war-imposed restrictions on the publication of all technical information related to the war effort, the mass of technical and scientific data accumulated in the development and manufacture of synthetic

polymers in the United States during the war began to appear on the program of this meeting.

The headquarters of the Division were at the Ambassador Hotel. The technical sessions were held in Convention Hall, with Chairman W. A. Gibbons presiding. The local arrangements for this meeting were ably handled by Harry Bimmerman and his committee, composed of Sam Martin, Larry Youse, William Ayscue and William Dunlap, Jr. Registration of members of the Division was about 1,000, with a total reservation for the Society in the neighborhood of 8,500.

Chairman Gibbons, in opening the technical sessions, reviewed the influence of World War II on the development of the rubber industry in the United States, and lauded the chemists and engineers of that industry for their contribution to this development. The following program of technical papers was presented:

1. W. A. Gibbons. Introduction.
2. C. F. Fryling. Purification and Emulsion Copolymerization of Isoprene.
3. H. W. Starkweather, A. S. Cater, F. B. Hill, Jr., V. R. Hurka, F. A. Saunders, H. W. Walker and M. A. Youker. Emulsion Polymerization of Diene Hydrocarbons.
4. T. J. Dietz, W. C. Mast, R. L. Dean and C. H. Fisher. Properties of Lactoprene-EV.
5. P. O. Powers. Copolymers of Dimethyl Styrene and of Vinyl Fatty Acid Esters with Butadiene.
6. C. M. Doede, G. DiNorscia and A. Panagrossi. Some Properties of Silastic at Elevated Temperatures.
7. W. S. Coe and J. L. Brady. Improved Types of GR-S Using Rosin Soap as an Emulsifier.
8. J. J. Owen, C. T. Steele, P. T. Parker, E. W. Carrier. Continuous Buna-S Preparation.
9. D. L. Schoene, A. J. Green, E. R. Burns, G. R. Vila. Development of a Better Processing GR-S.
10. R. L. Zapp and F. P. Baldwin. The Effect of Polymolecularity on the Deformation Characteristics of Butyl Polymers.
11. B. L. Johnson. The Effect of Molecular-Weight Distribution on the Physical Properties of Natural and Synthetic Polymers.
12. A. M. Borders and R. D. Juve. Correlation of Tensile Strength with the Brittle Points of Vulcanized Diene Polymers.
13. D. W. Scott. Osmotic Pressure Measurements with Polydimethylsilicone Fractions.
14. W. O. Baker and N. R. Pape. x-Ray Fine Structure of Synthetic Rubbers.
15. Charles Goodyear Lecture by Waldo L. Semon.
16. S. R. Olsen, C. M. Hull and W. G. France. The Sulfur Bond in Vulcanizates I. Implications of Halogen Reactions.
17. C. M. Hull, S. R. Olsen and W. G. France. The Sulfur Bond in Vulcanizates. II. Mineral Sulfide as an Index of Disulfide Cross-Bonding.
18. Milton L. Selker and A. R. Kemp. Sulfur Linkage in Vulcanized Rubber. III. The Reaction of Sulfur with 2-Methyl-2-butene.
19. A. P. Stubbs and C. R. Johnson. Balancing the Vulcanization of GR-S and Natural Rubber in GR-S Rubber Mixtures.

20. L. R. Sperberg, L. A. Bliss and J. F. Svetlik. Effect of Variable Black and Softener Quantities Upon the Physical Properties of a GR-S Compound. Part A. Philblack-A System at 1.75 per cent Sulfur.
21. R. E. Dobbin and R. P. Rossman. Mechanical Processing of Carbon Blacks and Resultant Effects in GR-S Compounds.
22. I. E. Lightbown, L. S. Verde and J. R. Brown, Jr. Butyl Inner Tubes—Performance and Influence on Tire Life.
23. A. M. Borders, R. D. Juve and L. D. Hess. Styrene-Diene Resins in Rubber Compounding.
24. Arnold R. Davis. Plasticizing GR-S and Natural Rubber.
25. F. D. Chittenden, C. D. McCleary and H. S. Smith. High-Solids Synthetic Latex Directly from the Reactor.
26. E. L. Borg, J. C. Madigan, R. L. Provost and R. E. Meeker. Continuous-Process Preparation of GR-S Masterbatches with Non-Black Pigments.
27. R. H. Walsh and I. W. Dobratz. The Effect of pH on the Physical Properties of Films from Synthetic Latices.
28. H. K. Livingston. The Creaming of Neoprene Latex.
29. G. E. P. Smith, Jr. and J. C. Ambelang. Alkyl Phenol Resins as Tackifiers for GR-S.
30. J. D. D'Ianni, F. J. Naples, J. W. Marsh and J. L. Zarney. Chemical Derivatives of Synthetic Rubbers.
31. John O. Cole and James E. Field. Fundamental Studies on the Oxidation of GR-S and Other Elastomers.
32. Hugh Winn, J. Reid Shelton and David Turnbull. The Role of Carbon in the Oxidation of GR-S Vulcanizates.
33. A. E. Juve. Crack Growth in GR-S Treads—Its Relation to State of Cure and Composition.
34. M. C. Throdahl. Dynamic Surface-Cracking of GR-S Vulcanizates in Ultraviolet Light.
35. J. Crabtree and A. R. Kemp. A New Accelerated Weathering Test for Rubber.
36. Don B. Forman and R. R. Radcliff. Measuring the State of Cure of Neoprene Vulcanizates.
37. L. T. Eby and F. W. Banes. Quantitative Determination of Inhibitors in Polymers by Ultraviolet Light Absorption.
38. R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell. Heats of Adsorption on Carbon Blacks.

In addition to its own program of papers, the Division participated in the High Polymer Forum, sponsored by the Division of Paint, Varnish and Plastics Chemistry and held jointly with the Divisions of Cellulose, Colloid, Organic, and Physical and Inorganic Chemistry. The Forum comprised the following papers:

1a. W. O. Baker and C. S. Fuller. Disorder in Linear Condensation Copolymer Solids.
1b. Frank R. Mayo. The Relative Activities of Ethylene Derivatives in Copolymerization.
1c. Turner Alfrey, Jr. Some Recent Results in the Field of Copolymerization.
1d. Frederick T. Wall. Partial Conversion Properties of Copolymers.

2. A. Goldberg, T. Alfrey and W. P. Hohenstein. Copolymerization of Vinyl Compounds with Dienes.
3. I. Skeist. Copolymerization. The Composition—Distribution Curve.
4. M. L. Huggins. The Viscosity of Dilute Solutions of Long-Chain Molecules. The Initial Concentration Dependence Constant.
5. C. Walling and E. R. Briggs. The Thermal Polymerization of Methyl Methacrylate.
6. P. Doty and E. Mishuck. The Temperature Dependence of the Osmotic Pressure of Polyvinyl Chloride Solutions.
7. W. D. Harkins. A General Theory of Emulsion Polymerization with Respect to Reaction Loci.
8. J. M. Grim, W. E. Baldwin, W. H. Hill. The Thermal Polymerization of 2-Vinylnaphthalene.
9. W. O. Baker and N. R. Pape. The x-Ray Fine Structure of Synthetic Rubbers.
10. E. L. Wittbecker, R. C. Houtz and W. W. Watkins. Elastic *N*-Substituted Polyamides.
11. R. A. Gregg and F. R. Mayo. Chain Transfer in the Polymerization of Styrene. II. The Reaction of Free Radicals with Carbon Tetrachloride.
12. R. D. Andrews and A. V. Tobolsky. Structural-Chemical Investigations of Rubbers by Stress Relaxation.
13. R. B. Mesrobian and A. V. Tobolsky. Degradation of Vinyl Polymers.

The Third Charles Goodyear Lecture, was presented by Waldo L. Semon, who chose as his subject "Research Leading to Commercial Butadiene Synthetic Rubber". Dr. Semon was voted this award in 1944, but because of the cancellation of the Fall Meeting of that year and both meetings in 1946, the presentation of his lecture was necessarily delayed until the present meeting.

At the business meeting held Thursday forenoon, John Blake, Chairman of the Nominating Committee, presented the following slate of nominees for officers for 1946–1947:

Chairman	W. W. Vogt
Vice-Chairman	H. E. Outcault
	R. A. Schatzel
Treasurer	C. W. Christensen
Secretary	C. R. Haynes
Sergeant-at-Arms	L. M. Baker
Directors	G. R. Cuthbertson
	G. L. Allison
	F. W. Frerichs*
	N. S. Grace
	S. D. Gehman
	W. J. Geldard
	A. M. Neal
	G. M. Swart

There were no further nominations from the floor, and the above slate has been submitted to the membership by letter ballot. Upon motion of J. T. Blake, C. R. Haynes was elected Assistant Secretary to relieve the retiring

* Mr. Frerichs has since resigned the nomination.

Secretary of a portion of his duties during the balance of the current year and, at the same time, to afford him the opportunity to become familiar with the various duties of his new office.

The chairman of the Membership Committee, H. E. Outcault, reported that his committee had succeeded in securing 228 new Members and 37 Associate Members since July, 1945. The present membership of the Division comprises:

Members	1,279
Associate Members	257
Total	1,536

The chairman of the Bibliography Committee, John McGavack, submitted a comprehensive report on the activities of his committee during the past two years. During that period this committee completed the compilation of a Bibliography of rubber literature for 1940–1941. This Bibliography will be distributed gratis to all members and associate members of the Division within the near future. It was voted subsequently by the Executive Committee that this Bibliography Committee be continued for another year and that the Division undertake at once the extension of the Bibliography for the years 1942–1943. Associated with Chairman McGavack in the work of this committee are M. E. Lerner, C. C. Davis and C. W. Christensen.

The Secretary reported that the revised By-Laws of the Division, evolved by a committee composed of H. E. Outcault, Chairman, and the Chairman and Secretary of the Division, had been approved by the membership in a letter ballot by the overwhelming vote of 558 to 7. The action of the membership was formalized by a vote of those in attendance at the meeting to adopt the revised By-Laws and to submit them to the Secretary of the Society for submission to the Council for final approval.

One of the principal changes incorporated in the new By-Laws is the addition of a section dealing with the Rubber Groups and their relationship to the Division. It provides for their sponsorship by the Division and for the election of one Director of the Division from the active membership of the Division located in the area served by each sponsored Rubber Group. Another significant revision provides that the Charles Goodyear Lecture Award shall be changed to the Charles Goodyear Medal.

The Divisional Banquet was held at the Chelsea Hotel Thursday evening, with about 850 members and guests in attendance. Bradley Dewey, President of the A. C. S., Charles L. Parsons, Retiring Secretary of the A. C. S., Alden H. Emery, Secretary of the A. C. S., and Walter H. Murphy, Editor of *Industrial and Engineering Chemistry*, were present as honored guests.

Continuing the custom initiated at the Spring 1944 Meeting in New York, the Officers of the Local Rubber Groups and the Officers and Directors of the Division held a joint luncheon on Friday noon. At this luncheon, the objectives of the new By-Laws with respect to the Rubber Groups were discussed. Consideration was given also to plans whereby more efficient scheduling of speakers before the various Groups might be effected. Any joint action dealing with this matter and other mutual problems affecting the Groups and the Division, will be under the direction of the Vice-Chairman of the Division, Walter Vogt.

H. I. CRAMER
Secretary

NEW BOOKS AND OTHER PUBLICATIONS

RUBBER RED BOOK.—1945 Edition, Fifth Issue. Published by *The Rubber Age*, 250 W. 57th St., New York 19, N. Y. Cloth, 6 by 9 inches, 692 pages. Price $5.—Although following about the same system of organization and classification as the 1943 edition, the new biennial issue of the directory of the rubber industry shows expansion of almost every section, with a total increase in pages of 112, including advertisements. Compiled and published under difficult production conditions, the book nevertheless presents a commendable coverage of data and information on the rubber industry. Practically every section of the book is still affected by wartime conditions, and many items as yet unavailable are listed for future reference on the return of more normal supplies and services. Included in the section on rubber reclaimers is a reprint of the Scrap Rubber Specifications of the Rubber Reclaimers Association, as revised September 21, 1945.

The following are the titles of sections in the book: rubber manufacturers in the U. S., classified alphabetically, by products, and by geographic location; rubber manufacturers in Canada; rubber machinery and equipment, listed by types, with manufacturers' names and addresses; accessories and fittings, with suppliers and their addresses; rubber chemicals and compounding materials, classified by types and trade or brand names, with suppliers listed; fabrics and textiles; natural rubber and related materials; synthetic rubbers and other rubberlike materials; reclaimed rubber; scrap rubber dealers; rubber latex, including latex compounds, water dispersions, miscellaneous products, compounding materials, machinery, and equipment; rubber derivatives; miscellaneous products and services, with new listings for coated material finishing, milling and mixing, rubber denuding, industrial sewing, washing crude rubber, and waterproofing fabrics; consulting technologists; manufacturers' representatives, sales agents, branch offices, etc.; technical journals; trade and technical organizations; "Who's Who in the Rubber Industry"; and a subject index. [From the *India Rubber World*.]

JOURNAL OF POLYMER SCIENCE. Editorial Board: P. M. Doty, R. Houwink, H. Mark, and C. C. Price. Interscience Publishers, Inc. and Elsevier Publishing Co., Inc., New York, N. Y. Bimonthly. 7¼ by 10¼ inches. Volume I, about 640 pages. Subscription, $8.50 per year. Foreign postage $1.00, including Canada. Issues 1 and 2.—This new journal, devoted to the advancement of fundamental knowledge on the physics and chemistry of polymers, offers to scientific workers in the field an opportunity to report experimental and theoretical contributions through a centralized medium. It will be the editorial policy to encourage freedom of discussion and to provide prompt publication.

Journal of Polymer Science will publish original papers, review articles, brief communications to the editors, and book reviews. The new journal is an outgrowth of, and a successor to, the *Polymer Bulletin*, which has ceased to appear.

The new journal reflects the consolidation of independent plans of the Elsevier Publishing Co., Inc., Amsterdam, Holland, and Interscience Publishers, Inc., New York to publish separate journals on the same topic. To avoid the coexistence of two journals devoted to the field of high polymers, the two publishers have coördinated their plans, and the outcome is the *Journal of Polymer Science*. Since these plans could not be realized before the appearance of

Issue 1, this issue was published under the title of the *Journal of Polymer Research;* but in the future there will exist only one journal, called the *Journal of Polymer Science.*

The Journal will be international in scope. A number of leading scientists in the field have been invited to form an advisory board, which represents all the important centers of polymer research in the United States and abroad, as well as scientific societies and their divisions whose fields of activity are within the scope of the journal. All papers will be published in the English language.

The publishers are willing to provide further information and supply sample copies on request. [From the *India Rubber World.*]

RUBBER. United States Tariff Commission, Washington, D. C. War Changes in Industry Series, Report No. 6. 104 pages.—This report on rubber, prepared in answer to requests of Congressional committees, was first issued in September, 1944, and the current edition does not differ substantially from the original report. In the section on world rubber industry in the prewar period appear discussions on the development and status of the industry in the various countries and on rubber prices and international control. The section on war changes in the United States covers imports and stockpiling of natural rubber, the synthetic rubber program, guayule, and the reclaimed rubber industry. The effects of the war on production in foreign areas are also considered. Finally there is a section on the postwar situation, which covers world consumption and production and the position of the U. S. rubber industry. Numerous tables show productions, exports, consumptions, U. S. synthetic rubber plant locations, capacities, costs, and prices. [From the *India Rubber World.*]

TIRE WEAR AND COST ON SELECTED ROADWAY SURFACES. (Bulletin No. 161 of the Iowa Engineering Experiment Station.) By R. A. Moyer and Glen L. Tesdall. Published by Iowa State College, Ames, Iowa. 6 x 9 in. 128 pp.—The factors which directly affect tire wear and cost, determined from the results of 450,000 miles of carefully controlled driving on gravel and bituminous surfaces and concrete pavements in Iowa, Kansas, Missouri, and Wyoming, are reported. The study is part of a general investigation of the effects of roadway surfaces on the costs of automobile operation, carried out from 1938 to 1942 in coöperation with the Public Roads Administration, and requiring detailed observations with eight cars driven at speeds ranging from 25 to 65 mph.

The results show that tire wear is influenced directly by 15 factors, the most important being car speed, roadway surface, and driving and maintenance habits of the operator, and that 12 factors, most of which are avoidable, contribute directly to tire-carcass failure. The average rate of tire wear observed on concrete pavements and bituminous surface indicates that, with due attention to tire maintenance, a life of 56,500 miles may be expected if speed does not exceed 35 mph., whereas at 65 mph. the life expectancy is only 18,700 miles. In the road trials the average life of ten tires operated on concrete pavements was 36,650 miles; that of twenty tires on gravel surfaces was 23,160 miles, many of these tires being retired because of carcass failures before the treads were worn smooth. Also, there were 98 punctures in 132,000 miles of travel on gravel surfaces, as compared to a single puncture in an equal distance on concrete pavements, and one puncture in 72,000 miles on bituminous surfaces.

The records show that tire wear on curves at speeds which cause the tires to "scream" is more than ten times the wear at speeds which do not result in sidewise skidding; that the tire costs in "stop-and-go" driving on concrete

pavements are slightly more than three times the corresponding costs for average country driving; and that many thousands of car-miles of tire use are lost through avoidable carcass failures. [From *The Rubber Age* of New York.]

COLLOID CHEMISTRY: THEORETICAL AND APPLIED. VOLUME VI. Edited by Jerome Alexander. Published by Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. 6 x 9 in. 1216 pp. $20.00.—The latest volume of this monumental work is divided into two parts, the first dealing with "General Principles and Specific Industries", the second with "Synthetic Polymers and Plastics". The two sections contain 70 papers, contributed by selected international specialists, 38 in the first and 32 in the second section. In addition, there is a general article on nuclear fission and atomic energy. As usual, there are excellent author and subject indexes.

The section on General Principles and Specific Industries contains several contributions of direct interest to the rubber chemist and technologist. These include "Rubber Latex Technology", by R. W. Albright and R. A. Lees; "Synthetic Rubber", by E. A. Hauser and D. S. Le Beau; and "The Comparative Behavior of Carbon Black in the Reinforcement of Natural and Synthetic Rubbers", by H. A. Braendle. The section on Synthetic Polymers and Plastics includes chapters on nitrocellulose, cellulose acetate, coumarone-indene resins, polythene, polystyrene, dichlorostyrenes and their polymers, vinylidene chloride polymers, acrylic resins, alkyd resins, nylon, silicones, chlorinated rubber, and synthetic resin adhesives in general. [From *The Rubber Age* of New York.]

ENCYCLOPEDIA OF HYDROCARBON COMPOUNDS. VOL. I. Compiled by Joseph E. Faraday. Available from Chemical Publishing Co., Inc., 26 Court St., Brooklyn 2, N. Y. 6½ x 9 in. Looseleaf. $15.00.—This is an American edition of Volume I of Faraday's extensive work on hydrocarbon compounds. It deals with hydrocarbons containing one to five carbon atoms and contains information relative to molecular formula, structural formula, occurrence in nature, names of the compounds, known methods of preparation (with complete bibliography), physical constants, methods of detection and determination, and outstanding properties and reactions. It is planned to issue new sheets every year. Since the volume is bound in looseleaf fashion, the new sheets can easily be inserted in the proper order for completing the volume with the latest developments. Sources of information used for the volume are Beilstein's *Handbuch der organischen Chemie* and its supplements and three of the chemical abstract journals, *Chemical Abstracts, British Chemical Abstracts, and Chemisches Zentralblatt.* Other volumes of the encyclopedia are planned at short intervals. [From *The Rubber Age* of New York.]

PHYSICAL CONSTANTS OF HYDROCARBONS. VOL. III. MONONUCLEAR AROMATIC HYDROCARBONS. By Gustav Egloff. Published by Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. 6 x 9 in. 661 pp. $15.00. (An A.C.S. Monograph).—This latest volume of "Physical Constants of Hydrocarbons", the third of the series, is a collation and evaluation of physical constants of mononuclear aromatic hydrocarbons. All data on melting point, boiling point, density and refractive index available before May, 1944, is included. Wartime restrictions, unfortunately, have prevented the incorporation of some valuable data determined under the auspices of the American Petroleum Institute at the National Bureau of Standards. The classification of "mono-

nuclear aromatic hydrocarbons" excludes hydrocarbons having a fused ring structure, any ring of which is aromatic. Biphenyl and bicycloheptylbenzene appear in the volume, but polynuclear aromatics, such as indane and tetralin, will appear in Volume IV. The constants of aliphatic and alicyclic hydrocarbons were published in Volumes I and II, respectively. The current volume is divided into 25 chapters, including an extensive introduction. [From *The Rubber Age* of New York.]

ABSTRACTS ON SYNTHETIC RUBBER (IN TWO PARTS): PART III—ARTICLES; PART IV—PATENTS. By Muriel E. Whalley. Issued by the National Research Council of Canada, Ottawa, Canada. 8½ x 11 in. each. Part III, 435 pp.; Part IV, 300 pp. $2.00 for each part.—These publications are a continuation of former work by the National Research Council of Canada on "Abstracts on Synthetic Rubber", Parts I and II of which were issued in 1943 (see *Rubber Age*, January, 1944, p. 366). As in the previous reports, the abstracts deal with the processes of manufacture of synthetic rubbers and related subjects, as well as the properties of the various synthetics and on work in connection with the improvement of such properties. Part III, which comprises 910 abstracts of articles arranged in alphabetical order by authors with a subject index, is a continuation of Part I, while Part IV, which consists of 501 abstracts of patents arranged in chronological order with a subject index, an index of patentees, and a numerical patent index arranged according to countries, is a continuation of Part II. In addition, Part IV contains a collection of 116 abstracts of patents seized by the Alien Property Custodian in the United States. Like the previous reports, the abstracts furnished are comprehensive. The source of each article is given in the case of articles, while the indexes are set off by the use of different colored paper, making them easy to locate and use. [From *The Rubber Age* of New York.]

ADVANCES IN COLLOID SCIENCE. VOL. II. SCIENTIFIC PROGRESS IN THE FIELD OF RUBBER AND SYNTHETIC ELASTOMERS. Edited by H. Mark and G. S. Whitby. Published by Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y. 6 x 9 in. 454 pp. $7.00.—As indicated by the title, this second volume in the series of "Advances in Colloid Science" covers the chemistry and physics of natural and synthetic rubber, and brings the scientific record up to date. The plan for this second volume was made by the late Elmer O. Kraemer, who felt that the quantity and importance of recent work in this field justified devoting an entire volume to it, a feeling with which rubber chemists and technologists will concur.

As in the first volume of this work (see *Rubber Age*, February, 1942, p. 384), the various sections are contributed by specialists in the field, both American and British. The current volume is divided into 9 sections, contributed by 13 authors. In addition, it includes an introduction by G. S. Whitby, one of the editors, and a biography of the late E. O. Kraemer. In an appendix, Hermann Mark, the other editor, briefly reviews some recent articles which are pertinent to the content of the various chapters of the book. Subject and author indexes are also included. Titles of the nine sections of the book, together with the authors of each, follow:

Second-Order Transition Effects in Rubber and Other High Polymers, R. F. Boyer and R. S. Spencer; *Crystallization Phenomena in Natural and Synthetic Rubbers*, Lawrence A. Wood; *The Study of Rubberlike Substances by x-Ray Diffraction Methods*, C. W. Bunn; *The Thermodynamic Study of Rubber Solu-*

tions and Gels, Geoffrey Gee; *Significance of Viscosity Measurements on Dilute Solutions of High Polymers*, R. H. Ewart; *The Kinetic Theory of Rubber Elasticity*, E. Guth, H. M. James and H. Mark; *Vulcanization*, E. Harold Farmer; *Rubber Photogels and Photovulcanizates*, Henry P. Stevens; *Reinforcing and Other Properties of Compounding Ingredients*, Donald Parkinson. Bibliographies appear at the end of each section. [From *The Rubber Age* of New York.]

A. S. T. M. STANDARDS ON RUBBER PRODUCTS; 1946. Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 x 9 in. 560 pp. $3.25.—Prepared by A.S.T.M. Committee D-11 on Rubber, this latest edition of the special compilation of standards on rubber and rubber-like materials is considerably larger than the previous one. It brings together in convenient form over 75 specifications and tests covering natural and synthetic rubbers.

Almost 200 pages are devoted to general methods—chemical analysis, identification and quantitative analysis of synthetic elastomers, sample preparation, tension testing, accelerated aging by the oxygen pressure and the oven methods, heat aging by the test-tube method, air-pressure heat test, resistance to light checking and cracking and resistance to accelerated light-aging of rubber compounds, cure adhesion, abrasion, tear, compression set, conditioning, changes in properties of rubber and rubber like materials in liquids, etc.

In the section on electrical tests, methods cover dielectric strength at commercial power frequencies, power factor and dielectric constant, and insulation resistance. The latest specifications for rubber and synthetic rubber compounds for automotive and aeronautical applications are included in another section. Thirteen specifications cover insulated wire and cable and other specifications and methods covering hose, belting, gloves, matting, tape, etc., are also given.

Miscellaneous tests include viscosity and total solids content of rubber cements, latices of natural and synthetic rubbers, asphalt composition of battery containers, rubber cups, cotton goods, cellular rubber products, adhesives, etc. There are four specifications and three methods covering non-rigid plastics, in addition to a section on nomenclature and definitions. [From *The Rubber Age* of New York.]

1945 SUPPLEMENT TO A.S.T.M. STANDARDS INCLUDING TENTATIVES. Part III. Non-Metallic Materials—General. American Society for Testing Materials, 260 S. Broad St., Philadelphia 2, Pa. Cloth, 6 by 9 inches. 518 pages. Price: members, $2.50; non-members, $4.—The Supplement contains the new and revised standards and tentatives in the nonmetallic general materials field that have been accepted since the appearance of the "1944 Book of Standards, Part III". Of the 24 standards 11 are newly adopted, and 13 are replacements of existing standards. Similarly, 27 of the 70 tentatives are replacements; the remaining 43 are published for the first time. The format is the same as that of previous issues, and there are subject and numerical indices.

For rubber are four standards: one for accelerated aging of vulcanized rubber by the oven method, and three tentative standards on natural rubber caps for use in hydraulic actuating cylinders, identification and quantitative analysis of synthetic elastomers, and conditioning of rubber and plastic materials for low-temperature testing. Included also are 13 specifications and standards for plastics, and seven specifications and methods of testing plastics used as electrical insulating materials. [From the *India Rubber World*.]

1946 MODERN PLASTICS ENCYCLOPEDIA. Published by the Plastics Catalogue Corp., 122 East 42nd St., New York 17, N. Y. 8 x 11 in. 1390 pp. $6.00, domestic; $7.00, Canada and Foreign.—Formerly called the *Plastics Catalog* and now properly termed the *Modern Plastics Encyclopedia*, the latest edition of this work has been completely revised and brought up-to-date to make it the most comprehensive guide available to the manufacture and use of plastics materials. The current edition is divided into 12 basic sections, including Plastics Panorama; Technical Data; Materials; Engineering Design; Molding, Extruding and Casting; Fabricating, Finishing and Assembly; Machinery and Equipment; Laminates and Vulcanized Fibre; Resin-Wood Products; Coatings; Synthetic Fibres; and Synthetic Rubber and Rubberlike Plastics. In addition, there is a bibliography on books and articles, a glossary giving the official definitions of technical plastics terms, and a directory section listing the names, addresses and personnel of all categories of plastics manufacturers. A series of 10 separate charts, covering plastics properties, solvents, plasticizers, etc., is furnished from the Encyclopedia. [From *The Rubber Age* of New York.]

HACKH'S CHEMICAL DICTIONARY (Third Edition). Edited by Julius Grant. Published by the Blakiston Co., 1012 Walnut St., Philadelphia 5, Penna. 6½ x 9½ in. 925 pp. $8.50.—Completely revised and brought up-to-date, the latest edition of this standard encyclopedic dictionary of modern chemical terms contains over 57,000 definitions. A feature of the dictionary is the numerous original tables of important data, diagrams, portraits, illustrations, and other well delineated aids, all designed to give a clear understanding of various subjects, including physics, astrophysics, geology, mineralogy, botany, etc. The various chain reactions are illustrated by formulas, and the periodic chain is fully tabulated, including complete scientific data down to Element 96. The latest data on atomic disintegration is included, together with brief, clear statements of the theories, laws and rules of chemistry, accurate descriptions of elements, compounds, drugs, minerals, etc., and biographic sketches of scientists who have contributed to the development and progress of chemistry. Nomenclature and spelling follow the system adopted by the American Chemical Society and British practices. [From *The Rubber Age* of New York.]

RECLAIMED RUBBER

RECLAIMED NATURAL RUBBER
" GR-S
" GR-I
" GR-N
" GR-M

A reclaim for every purpose.

Write for list and samples for your product.

PEQUANOC RUBBER CO.

BUTLER, NEW JERSEY

Main office and factory Butler, N. J.

New England Representative
Harold P. Fuller
203 Park Square Bldg.
Back Bay, Boston, Mass.

European Representative
Burnett & Co. (London) Ltd.
46 Herga Court
Harrow-on-the-Hill, Middlesex, Eng.

UNIFORM QUALITY
ZINC OXIDES
The Horse Head Brands

The New Jersey Zinc Company
160 Front Street
New York 7